

AMERICAN CHEMICAL JOURNAL

[Contributions from the Chemical Laboratory of Harvard College]

THE ACTION OF SODIC HYDROXIDE ON TETRABROMORTHOBENZOQUINONE¹

BY C. LORING JACKSON AND A. H. FISKE

In his wonderfully comprehensive paper² on tetrabrom-orthoquinone, Zincke states that a solution of sodic hydroxide converts it into an unstable green solid, which afterwards dissolves, forming the sodium salts of tetrabrompyrocatechin and what is probably a cyclopentenecarboxylic acid. A more detailed study of these reactions has shown the accuracy of his observations, although the action is not quite so simple as he thought.

The green solid formed at first decomposes spontaneously on standing with the alkali, or, if filtered out, as soon as it dries; and this instability, with its marked color, suggests that it may be closely related to the green or blue compounds³

¹ The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the Degree of Doctor of Philosophy by Augustus Henry Fiske.

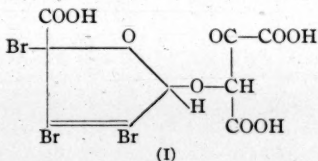
² Ber. d. chem. Ges., **20**, 1776 (1887).

³ Barth, Schreder: Monats. Chem., **4**, 176 (1883). Hantzsch, Herman: Ber. d. chem. Ges., **21**, 1754 (1888). Sworer: Chem. News, **60**, 1887 (1889). Nietzki, Schmidt: Ber. d. chem. Ges., **22**, 1653 (1889). Mazzara: *Ibid.*, **23**, 1390 (1890). Kehrman: J. prakt. Chem., [2] **43**, 260 (1891). Jackson, Grindley: THIS JOURNAL, **17**, 655 (1895). Astre: Compt. rend., **121**, 326, 530 (1895). Jackson, Torrey: THIS JOURNAL, **20**, 426 (1898). Imbert: Compt. rend., **126**, 529 (1898). Fischer, Wellmann: Ber. d. chem. Ges., **27**, 2384 (1904). Torrey, Hunter: J. Am. Chem. Soc., **34**, 705 (1912). Richter: Ber. d. chem. Ges., **43**, 3599 (1910).

which have been frequently observed when alkaline substances act on quinones. Torrey and Hunter have given reasons for supposing that some, at least, of these products are salts of quinhydrones, and the properties of our green solid were not at variance with this hypothesis. For instance, it yielded on acidification a mass easily soluble in alcohol, like the mixture of tetrabromopyrocatechin and tetrabromorthoquinone which would be formed from a quinhydrone; and the brown product formed by its spontaneous decomposition, although it resembled in appearance the ether $C_6Br_4O_2C_6Br_2(OH)_2$, was also too soluble in alcohol to be this compound. It was probably the expected mixture of tetrabromopyrocatechin and tetrabromorthoquinone, since the ether $C_6Br_4O_2C_6Br_2O_2$ was formed when it was treated with glacial acetic acid. According to the views developed later, if the green substance is the salt of the octobromorthoquinhydrone, its formation is due to a secondary reaction, and it is of no use in tracing the decomposition of tetrabromorthoquinone by sodic hydroxide and this is also true if we adopt the theory of Astre or of Richter.

To detect the real products of the action of sodic hydroxide on tetrabromorthoquinone we took up the study of the yellowish solution obtained by the further action of the alkali upon the green solid, which was the first product. This yielded on acidification a precipitate of tetrabrompyrocatechin, as already found by Zincke, and after this had been filtered off, extraction with ether gave an acid which differed according to the strength of the solution of sodic hydroxide used. A normal solution produced an acid melting at 217° , to which we assign provisionally the formula $C_{10}H_6Br_4O_9$. With a solution containing 60 grams to the liter two acids were obtained, one, $C_{10}H_5Br_5O_9$, melting at 207° , and one at 121° , of which we have as yet only bromine determinations, so that we give the formula $C_{10}H_5Br_5O_7$ with all possible reserve. Finally, with a solution containing 200 grams of sodic hydroxide in the liter the acid melted at 174° , and had the formula $C_{11}H_6Br_2O_9$. Of these acids only that melting at 207° has been studied with any approach to thoroughness, so we begin our discussion of their structural relations with this compound.

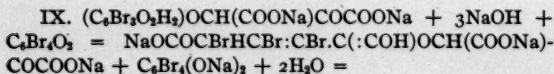
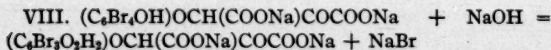
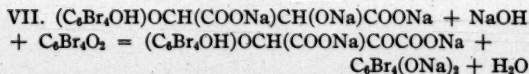
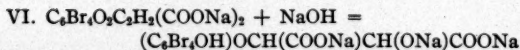
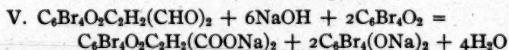
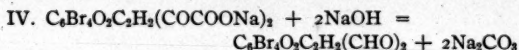
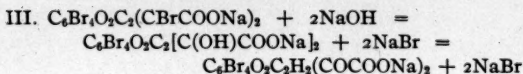
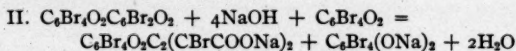
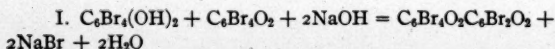
Our attempts to make out the constitution of the acid $C_{10}H_5Br_3O_9$, melting at 207° have led to four structural formulas in harmony with the observed facts. Of these, Formula I explains the observations most simply, and we have therefore adopted it as the best expression of our present knowledge of this compound, but much more experimental work will be necessary before its structure is finally established.

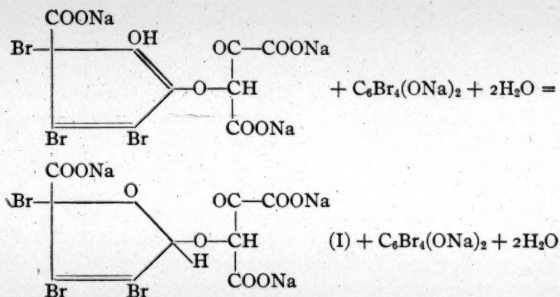


The other formulas, which require more strained hypotheses to bring them into harmony with the facts, will be discussed after we have given our reasons for preferring Formula I. According to this view of its structure the acid is the tribromomethylcyclopentene ether of oxalhydroxyacetic acid.

One of the strongest arguments for Formula I is that such a compound would be produced by the action of sodic hydroxide on tetrabromomethoxyquinone by a series of reactions, each of which is the one to be expected under such conditions; we shall therefore give these reactions in detail. In forming an acid with 10 atoms of carbon from tetrabromomethoxyquinone, $C_6Br_4O_2$, two molecules of this substance must be united in some way, and the most probable attachment is one by the oxygen forming in the first place the ether $C_6Br_4O_2C_6Br_2O_2$, which is easily produced by the action of tetrabromopyrocatechin on tetrabromomethoxyquinone. We are here met with the difficulty of forming the small amount of tetrabromopyrocatechin necessary to start Reaction I. After the reactions have begun, more than enough of this body will be formed to continue the action to an end; in fact, as already stated, a considerable excess of it is left after the reactions are finished. We have tried to meet this difficulty by supposing a reaction similar to that of sodic hydroxide on benzaldehyde, giving the tetra-

bromopyrocatechin needed and some acid, but, as this first action will be superseded at once by Reactions I-IX, this suppositious acid will be formed in such small quantity that it would naturally be overlooked among the secondary products, unless, indeed, it was decomposed by further action of the sodic hydroxide. The tetrabromopyrocatechin for starting Reaction I once obtained, the acid with Formula I is produced as follows:





Some quantitative experiments which give a certain amount of support to these reactions, and a possible objection to Reaction II, will be discussed near the end of this introduction.

The second argument in favor of Formula I is based on the most striking reaction of our acid, that of bromine on a strong aqueous solution of it, which yielded 3 molecules of carbonic dioxide for each molecule of the acid, a little oxalic acid, and a substance melting at 97° - 98° . The 3 molecules of carbonic dioxide would be expected from the decomposition of the 3 carboxyl groups in Formula I, and the oxalic acid would be the natural product from the two atoms of carbon remaining in the oxalhydroxyacetic side chain, after it had lost its two carboxyls. The amount of oxalic acid obtained was smaller than would be expected on this theory, but this is accounted for by its decomposition during the evaporation of the solution containing an excess of bromine.¹ The substance melting at 97° - 98° was proved to be the heptabrommethylidiacetyl, $\text{CBr}_3\text{CHBrCOCOCBr}_3$, which would be formed from an acid with Formula I by the introduction of 4 atoms of bromine between the two atoms of carbon now carrying bromine alone, the loss of carbonic dioxide by the carboxyl groups and the removal by oxidation of the residue left after the destruction of the side chain.

¹ No attempt was made to collect any carbonic dioxide formed during this evaporation, the 3 molecules of carbonic dioxide mentioned above being given off during the reaction in the cold.

The proof that the substance melting at 97° – 98° had the formula $\text{CBr}_3\text{CHBrCOCOCBr}_3$ was given by the action of sodic carbonate in aqueous solution upon it, which yielded 2 molecules of bromoform, one of sodic oxalate, and one of sodic bromide for each molecule of the substance. We also expected formaldehyde or formic acid from the $-\text{CHBr}-$ group, but were unable to find it in spite of many attempts. When the substance was heated to 100° in a sealed tube with water, an organic compound described later was the principal product, and small amounts of bromoform, hydrobromic acid, and oxalic acid were formed, showing a decomposition similar to that with sodic carbonate, but it was of especial interest that in this case they were accompanied by carbonic dioxide, probably resulting from the $-\text{CHBr}-$ group, whose decomposition product had escaped us in the experiments with sodic carbonate, as must have been the case if it consisted of carbonic dioxide.

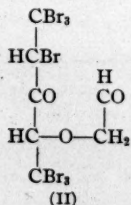
When trying to identify the bromoform obtained in this reaction we were confronted with one of those cases not uncommon in organic research, where it is necessary to study a liquid that can be prepared in quantity sufficient for the ordinary methods of manipulation only with a great expenditure of time and labor. For instance, if we dried our specimen (obtained from several experiments) with a dehydrating agent, the loss would reduce it below the amount necessary for analysis, and drying *in vacuo* was impossible because of its volatility. Accordingly, we used successfully the method of drying by wiping with moist filter paper devised by us¹ for such cases. Again, it was impossible with so little substance to obtain a boiling point accurate enough to characterize it, and to meet this difficulty a method of identification was contrived by one of us (Fiske), which gave an excellent result even with this small quantity, and so far as we can find is new. It seems to us a valuable addition to the resources of the organic chemist in cases of this sort. The process consists in determining the vapor pressure of the oily liquid by distilling it with a few drops of water, and observing the boiling point,

¹ THIS JOURNAL, 44, 439 (1910).

which can be determined with sufficient accuracy with this larger amount of liquid. The vapor pressure of water at this temperature was then subtracted from the barometric pressure, leaving the vapor pressure of the other liquid, which was compared with that calculated for the supposed compound. In our experiment the boiling point was found to be 93° – 94° , which gave as the vapor pressure of the oil 163 mm., while the vapor pressure of bromoform at 93° – 94° was determined from the observations of Kahlbaum and Thorpe to be between 162 and 164 mm.

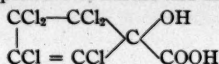
Our inference that the substance melting at 97° – 98° is the heptabrommethyldiacetyl was confirmed by its showing the yellow color characteristic of 1,2-diketones, which disappeared when a derivative was formed affecting the keto groups, such as, for instance, the hemiacetals with alcohols. Other confirmatory observations were the formation of oxamide when the body was treated with ammonia, of oxanilide with aniline, and of ethyl oxalate, probably the mono ester, when the ethyl hemiacetal was decomposed by water at 100° . On the other hand we could obtain neither an oxime nor a hydrazone from this diketone, but that is not strange, as these reactions generally fail with ketones loaded with negative radicals.

In addition to the two principal arguments for assigning Formula I to the acid melting at 207° the following observations tell in favor of this formula. By the less energetic action of bromine and water on the acid a product melting at 96° – 97° is obtained, which upon analysis gave results corresponding to the formula



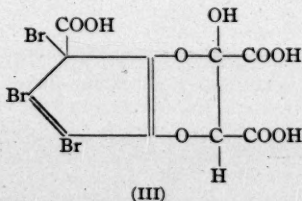
Unfortunately we have not had time to test this structure by further experiments, but two observations give it a certain confirmation. The substance is white instead of being yellow like the heptabrommethylodiacetyl, and on exposure to the air it turns brown, which may be due to an oxidation of the aldehyde group. Sodium carbonate in aqueous solution causes the replacement of one of the atoms of bromine by a hydroxyl group, giving a compound, $C_7H_4Br_6O_4$, melting at $71^\circ-72^\circ$, instead of decomposing it completely, as it does the substituted diacetyl.

The acid melting at 207° is tribasic as required by Formula I, and its salts are so unstable that they are decomposed even by the spontaneous evaporation of their aqueous solutions, as would be expected from a derivative of the yet unprepared oxalhydroxyacetic acid. Also the difficulty in isolating these salts recalls the experience of Zincke and Kuster¹ with the acid

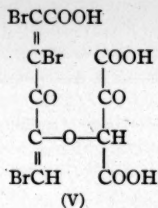
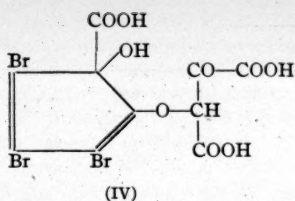


which in some respects is like the cyclopentene ring of Formula I. We succeeded in preparing in a pure state only the monopyridine salt made without the use of water, and it is worth noting that our formula shows a difference between one of the carboxyls and the other two, which might well lead to a mono salt. In fact, our observations agree with Formula I with the single exception that boiling the acid with strong hydrobromic acid for 8 hours leaves it unaltered.

In addition to Formula I we have worked out three others, which explain the reactions of our acid melting at 207° , but



¹ Ber. d. chem. Ges., **31**, 2719; **33**, 812.



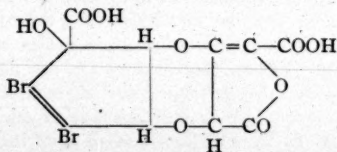
we prefer (I) for the following reasons: It seems to us that the hydroxyl group in (III) could be formed only by a much less probable reaction than any of those given in Reactions I-IX, and, further, such a compound should give an acet derivative with acetyl chloride, whereas our acid is not affected by this reagent. (IV) is attractive from its analogy to the cyclopentenehydroxy acids usually formed by the breaking down of a six-carbon ring,¹ but it shares with (III) the objection that it should form an acet compound, and also it is probable that with bromine and water it would give $\text{CBr}_3\text{CBr}_2\text{COCOCBr}_3$ rather than the actual product $\text{CBr}_3\text{CHBrCOCOCBr}_3$. To be sure, this compound could be formed, if hydrobromic acid were added as well as bromine, but this seems to us improbable when bromine, as here, is in great excess. This last objection also applies to (V) and the conversion of the CHBr_2 groups into CBr_3 makes the decomposition of such a body with bromine and water less simple than that of one constituted as in Formula I. It will be observed that none of these objections are strong enough to lead to the rejection of these formulas, but they seem to us to leave (I) as the simplest explanation of the observed facts, which is all we claim for it.

The heptabrommethyl diacetyl, $\text{CBr}_3\text{CHBrCOCOCBr}_3$, combines with methyl alcohol in the cold to form the monomethyl hemiacetal, $\text{CBr}_3\text{CHBrC(OH)(OCH}_3\text{)COCBr}_3$, melting at $100^\circ\text{--}101^\circ$; and with ethyl alcohol the corresponding com-

¹ For instance, Zincke: Ber. d. chem. Ges., 19, 2509 (1886). Zincke, Kuster: *Ibid.*, 26, 2104 (1893).

pound, $\text{CBr}_3\text{CHBrC}(\text{OH})(\text{OC}_2\text{H}_5)\text{COCBr}_3$, melting at $93^\circ\text{--}94^\circ$. The position of the hemiacetal group has not been determined. The ethyl compound, when heated with water to 100° in a sealed tube, yielded an oil, which, after it had been freed from bromoform, distilled at about the boiling point of diethyl-oxalic ester, and therefore was probably the expected mono-ethyl ester, which is converted into the diethyl compound by distillation.

Of the three other acids, that melting at 174° has been the most thoroughly studied, and, although the work has not gone far, we have discovered a formula for it which accounts for the known facts and agrees so well with that proposed for the acid melting at 207° that we feel justified in adopting it provisionally, although we can bring no proof of its correctness. This acid melting at 174° has the formula $\text{C}_{11}\text{H}_8\text{Br}_2\text{O}_9$, and when treated with bromine and water gives the heptabrommethyl-diacetyl obtained from the acid melting at 207° ; it is fair to assume, therefore, that both contain a similar group, the five-carbon ring of Formula I. From this assumption the structure (VI) is easily developed, in which the side chain con-



(VI)

sists of a carboxylactone, and the substance is the dibromohydroxycarboxylcyclopentene orthodiether of carboxyldihydroxyisocrotonlactone. It was proved to be tribasic by titration with sodic hydroxide, which might well saponify such a lactone, whereas with baric carbonate the salt of a dibasic acid was obtained, in harmony with Formula VI. The salts of this acid were unstable like those of the acid melting at 207° and this would be expected of (VI), on the one hand in view of the work of Zincke and Kuster cited above, and on the

other since the lactone on saponification would give an unsaturated hydroxyl acid dropping at once into a comparatively unstable α -keto acid. In forming the heptabrommethyldiacetyl from it by the action of bromine and water the action would be similar to that already given under the acid melting at 207° , with the addition of the conversion of the hydroxyl into bromine by the hydrobromic acid formed in the previous reactions. The lactone might well resist the milder action of bromine, and therefore not give the white compound $\text{CBr}_3\text{CHBrCOCH}(\text{OC}_2\text{H}_5\text{O})\text{CBr}_3$, melting at 96° - 97° , obtained in this way from the 207° acid.

The formation of an acid of Formula VI from tetrabromorthoquinone may be explained by reactions similar to I-IX, on the supposition that the more reactive stronger alkali carries the action on one branch of the side chain (Reactions III, IV, V) to the formation of the final carboxyl group, before the second branch has had time to be attacked, giving the compound $\text{C}_6\text{Br}_4\text{O}_2\text{C}_2\text{H}(\text{CBrCOONa})(\text{COONa})$, when the lactone would be formed by the reaction of the sodium in the COONa group with the bromine in the γ position.

We can say little about the constitution of the two remaining acids. Even the empirical formula of that melting at 121° is still doubtful, as the mother liquors, in which it was found occasionally, yielded enough of it only for some determinations of bromine. The formula of the acid melting at 217° rests on a safer basis, as the bromine determinations were confirmed by a determination of calcium in the calcium salt, which also showed the acid to be dibasic. While more analytical work is necessary before the formula $\text{C}_{10}\text{H}_6\text{Br}_4\text{O}_9$ can be finally accepted, we have observed a few facts which throw some light on its constitution. It is distinctly whiter than the two acids melting at 207° and 174° , and, when treated with bromine and water, it gave a white substance melting at 156° instead of the yellow heptabrommethyldiacetyl melting at 97° - 98° ; we therefore think it probable that it does not contain the cyclopentene group of Formulas I and VI, but that in it the benzene ring may exist unaltered, and this view is supported by the large amount of bromine (4 atoms) which it contains,

and the fact that it is formed when weak solutions of the alkali are used.

Whenever the decomposition of the tetrabromorthoquinone was carried on with a weak solution of sodic hydroxide, an oil appeared in addition to the solid acids. We did not have time to attempt the identification of this oil—at best a very difficult task—but a series of quantitative experiments with a fifth-normal solution of potassic hydroxide may throw some light on its relationships. In the following table the experimental results ("Found") are compared with the amounts of potassic hydroxide, carbonic dioxide and potassic bromide required by Reactions I-IX ("Calculated"). The quantities are given in numbers of molecules.

CaBr ₂ O ₃	Calculated		Found	
	7			
KOH	22	24.0	22.92	23.18
CO ₂	2	2.62	1.84	1.85
KBr	5		14.3	14.3

The agreement between these experimental results is much closer than we expected, considering possible secondary reactions, and, if it is not due to accidental coincidences, seems to us to justify the conclusion that the two products (the acid melting at 217° and the oil) are formed principally by the same series of reactions, for, if there were two parallel series, it is hardly possible that such close agreements would be obtained in three series of experiments, in which no special care was taken to secure the same conditions. The agreement of the observed amounts of potassic hydroxide and carbonic dioxide with those required by Reactions I-IX for making the acid melting at 207° would indicate that the series of reactions mentioned above is identical with these so far as the use of potassic hydroxide and the formation of carbonic dioxide are concerned, the acid melting at 217° proceeding from only part of them, and the oils probably being formed from the two solid acids by the replacement of bromine, owing to the action of the potassic tetrabrompyrocatechin present in large quantity in the solution, thus forming the excess of potassic bromide, which amounts to nearly 3 times that given by the formation

of the acid melting at 207° . The agreement between the observed quantities and those required for Reactions I-IX except in the case of the potassic bromide furnishes a welcome confirmation of these reactions.

Some experiments with tetrabromorthoquinone and reagents other than sodic hydroxide showed that potassic or ammoniac hydroxide acted in essentially the same way as sodic hydroxide; baric hydroxide seemed to give only the differences to be expected from the insolubility of the barium salt of tetrabrompyrocatechin, but plumbic hydroxide had no action. Sodic or acid sodic carbonate also seemed to behave like sodic hydroxide, giving the unstable green product, some of the acids described above, and in addition bromanilic acid. At first we supposed this new product to be formed from the tetrabrompyrocatechin, but this could not be the case, as special experiments showed that this compound is not decomposed under any conditions by solutions even of sodic hydroxide weaker than twice normal, and this twice normal solution forms bromanilic acid with it only when boiling. On the other hand the red ether $C_6Br_4O_2C_6Br_2O_2$ yields bromanilic acid with a twice normal solution of sodic hydroxide after standing for two days in the cold, so that here is the probable source of this product in the experiments mentioned above. This action, however, is a slow one, as even after heating tetrabromorthoquinone with a solution of sodic hydroxide for an hour there was left 1 gram of the ether $C_6Br_4O_2C_6Br_2O_2$ from 5 grams of the orthoquinone.

In Reaction II we represent the red ether as decomposed by sodic hydroxide in a different way from the saponification mentioned above, but we think this difference is sufficiently explained by the presence of the oxidizing agent (tetrabromorthoquinone). Under these circumstances Reaction II might take place so much more rapidly than the rather sluggish saponification of the ether that no bromanilic acid would be formed. This hypothesis is supported by the fact that the bromanilic acid appears as a secondary product only, when the reactions are carried on with milder alkaline reagents, such as baric hydroxide, sodic carbonate, or acid sodic carbon-

ate, which need to stand for some time with the tetrabrom-orthoquinone to form our acids.

EXPERIMENTAL

ACTION OF ALKALINE SOLUTIONS ON TETRABROMORTHOBENZO-QUINONE

The Green Preliminary Product

The first visible effect of an alkaline solution on tetrabrom-orthoquinone was the formation of a green solid, which, however, was very unstable, as, if sodic hydroxide was used, it disappeared often in as short a time as 10 minutes, forming a yellowish liquid. With a solution of sodic carbonate the green product acted less quickly, some specimens retaining their color for as much as two days, but finally, in this case, also, it decomposed partly into the yellowish solution, partly into a brown solid. In trying to prepare the green substance we used, therefore, a half normal solution of sodic carbonate with the tetrabromorthoquinone dissolved in benzene and poured upon the alkaline liquid. A green line soon appeared at the junction of the two liquids, and the precipitate, as it formed, fell through the aqueous liquid, and collected on the bottom of the vessel. The product obtained in this way was free from imprisoned tetrabromorthoquinone, which was always present, when, as in most of our experiments, the alkaline liquid acted on the solid quinone. A green specimen (containing imprisoned orthoquinone) was filtered out, washed with a little water, which removed bromanilic acid, and allowed to dry on a porous plate. As soon as it became fairly dry, brown spots appeared, which gradually spread throughout the entire mass. This behavior recalls the sodium salt of tribromoresorcin,¹ which decomposed spontaneously in a similar way. A portion, which had not lost its green color, was acidified with hydrochloric acid, when it was converted into a reddish brown solid easily soluble in alcohol. Of the products which would be expected from this reaction, this solubility is in harmony with tetrabromorthoquinone and tetrabrompyrocatechin, whereas the ethers $C_6Br_4O_2C_6Br_2O_2$

¹ THIS JOURNAL, 18, 117 (1896).

and $C_6Br_4O_2C_6Br_2(OH)_2$ could hardly be present, as they are only slightly soluble in alcohol.

We also tried the following experiments on the brown solid formed by the spontaneous decomposition of the green product. A specimen of it dissolved freely in alcohol, and water threw down from the solution a dull reddish brown precipitate. Another specimen, prepared by the benzene method, and therefore free from imprisoned orthoquinone, was washed with water, to which it gave up a quantity of sodic bromanilate, and then treated with hot glacial acetic acid, which dissolved most of it, but left a residue, evidently the ether $C_6Br_4O_2C_6Br_2O_2$ from its brilliant red color and essential insolubility in common solvents. The acetic acid solution contained much tetrabrompyrocatechin. These observations indicate that the brown product is principally tetrabrompyrocatechin with some tetrabromorthoquinone, and this view is supported by the observation that much of the ether $C_6Br_4O_2C_6Br_2O_2$ was formed by the action of nitric acid on the brown product. Neither the red ether $C_6Br_4O_2C_6Br_2O_2$ nor the brown one $C_6Br_4O_2C_6Br_2(OH)_2$ can exist in any quantity already formed in this brown substance, because, as stated earlier, it is easily soluble in alcohol.

Final Products of the Action of Sodid Hydroxide

After the green solid formed at first had disappeared, the product of the action of sodic hydroxide on tetrabromorthoquinone was a slightly yellow solution, and this on acidification with hydrochloric acid deposited a precipitate, which, as Zincke¹ states, is tetrabrompyrocatechin, since on recrystallization from hot glacial acetic acid it showed the constant melting point 190° – 191° instead of 191° – 192° and an analysis gave 75.39 per cent. of bromine, whereas $C_6Br_4(OH)_2$ contains 75.11 per cent. Further, when treated in alcoholic solution with fuming nitric acid and glacial acetic acid, it gave a red crystalline product melting at 146° – 147° , the melting point of the crude tetrabromorthoquinone prepared in this way, and sodic hydroxide gave with this the characteristic green color.

¹ Ber. d. chem. Ges., **20**, 1776 (1887).

The filtrate from the tetrabrompyrocatechin gave on extraction with ether one or more acids, the product differing according to the conditions under which it was formed; thus, a normal solution yielded an acid melting at 217° ; from one containing 60 grams of sodic hydroxide in the liter two acids were obtained, one melting at 207° , the other at 121° ; while, if the solution contained 200 grams of sodic hydroxide in the liter, the resultant acid melted at 174° . These were the usual products when solutions of the strength given were used, but on 3 occasions exceptional results were obtained; thus, once a solution containing 200 grams of sodic hydroxide to the liter gave almost entirely the acid melting at 207° instead of that melting at 174° (we cannot explain this, unless it were due to the difference in temperature between winter and spring); and on two occasions the acid melting at 174° was obtained with the weaker solutions, which usually gave the other acids; of these one was with a half normal solution cooled to 4° ; the other was when a half normal solution was used with a benzene solution of tetrabromorthoquinone instead of with the dry powder.

An account of our study of the effects of other conditions and reagents on the product will be found after the descriptions of the four acids, which we begin with that melting at 207° , as this is the only one which we have been able to study at length in the time at our disposal.

Acid Melting at 207° . Tribromcarboxylketocyclopentene Ether of Oxalhydroxyacetic Acid

Twenty grams of tetrabromorthoquinone were mixed with one liter of a solution containing 60 grams of sodic hydroxide, and the mixture allowed to stand at the temperature of the room with occasional shaking, till all of the green precipitate formed at first had dissolved. The solution was then poured into a beaker containing a little more than the amount of strong hydrochloric acid required for the neutralization of the alkali, and the precipitate allowed to settle overnight, as this facilitated the filtration. After this tetrabrompyrocatechin had been removed, the filtrate was extracted with ether most conveniently

in the apparatus invented by one of us.¹ The ether extract on spontaneous evaporation left a yellow crystalline residue mixed with an oil (discussed later in this paper), and this, after standing on a porous plate, was boiled repeatedly with successive portions of benzene, from which on cooling the acid separated as a yellow flocculent precipitate. It was washed with cold benzene, and then purified by recrystallization from hot benzene, until it showed the constant melting point 207° , when it was dried *in vacuo* for analysis.

I. 0.3383 gram substance gave 0.2930 gram CO_2 , 0.0343 gram H_2O .

II. 0.2258 gram substance gave 0.1961 gram CO_2 , 0.0237 gram H_2O .

III. 0.1330 gram substance gave 0.1477 gram AgBr.

IV. 0.2224 gram substance gave 0.2460 gram AgBr.

	Calculated for $\text{C}_{10}\text{H}_5\text{Br}_3\text{O}_4$	I	II	Found	III	IV
C	23.58	23.62	23.69			
H	0.98	1.13	1.17			
Br	47.16				47.25	47.06

Properties of Tribromcarboxylketocyclopentene Ether of Oxalhydroxyacetic Acid.—It crystallizes from benzene in flocculent masses of pale yellow needles, which melt with decomposition at 207° . It is easily soluble in water, alcohol, methyl alcohol, ether, chloroform, ethyl acetate or glacial acetic acid, slightly soluble in cold benzene, more freely in hot, almost insoluble in ligroin. Benzene is the best solvent for it. The aqueous solution decomposes carbonates with effervescence. The basicity of the acid was determined by titration with fifth-normal potassic hydroxide solution, phenolphthalein being used as the indicator.

I. 0.3258 gram substance required 10.24 cc. of the solution containing 0.0800 gram K.

II. 0.6687 gram substance required 20.88 cc. containing 0.1633 gram K.

	Calculated for $\text{C}_{10}\text{H}_5\text{Br}_3\text{K}_3\text{O}_4$	I	Found	II
K	19.11	19.70		19.63

The acid is therefore tribasic.

¹ Fiske: *THIS JOURNAL*, 41, 510 (1909).

Many attempts were made to prepare salts of the acid, but none were obtained in a pure state except a monopyridine salt described later. The solutions prepared by the action of the acid on a hydroxide or carbonate decomposed on evaporation, as shown by the appearance of a brown color, even when the evaporation was carried on at ordinary temperatures. The sodium salt and the calcium salt prepared from the carbonates gave no products worth analysis. The barium salt was prepared from the hydroxide and acid in aqueous solution, removing the excess of baric hydroxide with carbonic dioxide, and heating to drive off the excess of carbonic dioxide. The filtrate was then allowed to evaporate spontaneously, and the salt analyzed.

0.0910 gram of salt gave 0.0468 gram BaSO_4 .

	Calculated for $\text{Ba}_2(\text{C}_{10}\text{H}_3\text{Br}_2\text{O}_9)_2$	Found
Ba	28.97	30.24

This, so far as it goes, confirms the results from the titrations.

An attempt to prepare an ammonium salt with aqueous ammoniac hydroxide gave what seemed to be a compound $\text{C}_{10}\text{H}_3(\text{NH}_4)_3\text{Br}_2\text{NH}_2\text{O}_9$, the bromine found differing from the theoretical by about 2 per cent.

We next tried to prepare salts without the use of water. On dissolving the acid in an excess of pyridine, and diluting with ether, yellow, feathery flakes were precipitated, which, after thorough washing with ether, melted at 122° – 123° , and were dried *in vacuo* for analysis.

I. 0.1168 gram substance gave 0.1113 gram AgBr .

II. 0.1005 gram substance gave 0.0943 gram AgBr .

	Calculated for $\text{C}_{10}\text{H}_3(\text{C}_5\text{H}_5\text{N})\text{Br}_2\text{O}_9$	I	Found	II
Br	40.82	40.54		39.94

The substance is therefore the monopyridine salt. It forms yellow, feathery flakes which melt at 122° – 123° , and are insoluble in ether or benzene.

A phenylhydrazine salt made by mixing benzene solutions of the acid and phenylhydrazine came down as a pale yellow

precipitate, but gave results on analysis between those for a mono and a di salt.

Aniline had no apparent action on a benzene solution of the acid. Sodid methylate seemed to have no action in the cold, as no sodid bromide was formed, but if heated with the acid, a test for bromide was obtained. When the acid was boiled with a twice normal solution of sodid hydroxide, a dark reddish solution was obtained, which gave a test for sodid bromide. In the time we could give to this work we did not succeed in isolating the organic product, but on treating the solution with bromine and water a yellow precipitate was formed, which after purification melted at 97° , and was therefore undoubtedly the heptabrommethyldiacetyl, formed by the action of bromine and water on the original acid melting at 207° as described later. The sodid hydroxide therefore seems not to have effected a far-reaching decomposition, but to have converted the acid into a related substance containing less bromine. Strong hydrobromic acid was boiled with the acid for 8 hours, and the original substance was recovered unaltered. Phosphoric pentabromide seemed to act on the substance, but the product was so uninviting that the work was not continued. Acetic anhydride, acetyl chloride, or benzoyl chloride in the Baumann-Schotten reaction either had no action, or produced far-reaching decompositions of the acid.

Action of Bromine and Water on the Tribromcarboxylketocyclopentene Ether of Oxalhydroxyacetic Acid

When a concentrated aqueous solution of the acid melting at 207° was mixed with bromine, and heated, a heavy, yellow precipitate was formed, which melted to a clear yellow oil. The reaction was accompanied by evolution of carbonic dioxide, the amount of which was determined by collection in a baric hydroxide solution, and weighing the baric carbonate formed:

- I. 0.6687 gram acid gave 0.7531 gram BaCO_3 .
- II. 1.3800 grams acid gave 1.7068 grams BaCO_3 .
- III. 0.4984 gram acid gave 0.5916 gram BaCO_3 .

	Calculated for 3 molecules of CO ₂	I	Found II	III
CO ₂	25.98	25.16	27.62	26.51

It is evident, therefore, that each molecule of the acid gave off three molecules of carbonic dioxide. Oxalic acid was detected in the aqueous liquid but in small quantity, as it left only an insignificant residue on evaporation. The yellow oil, which solidified on cooling to an orange-yellow crystalline product, was recrystallized from naphtha until it showed the constant melting point 97° – 98° .¹ This substance was most conveniently prepared in quantity direct from the orthoquinone as follows: 200 grams of sodic hydroxide were dissolved in a liter of water, cooled to a few degrees above zero, and treated with 100 grams of tetrabromorthoquinone, which were added in small portions at a time with constant shaking. These are the conditions for making the acid melting at 174° , which gives this same bromine derivative. The dark solution with a brown precipitate was allowed to stand several hours to complete the reaction, and was then poured into a beaker containing about 300 cc. of strong hydrochloric acid, which was somewhat more than enough to neutralize the alkali. The mixture was allowed to stand overnight, as this made it easier to filter off the tetrabrompyrocatechin, and after this had been removed, the filtrate in a two-liter flask was treated with 5 cc. of liquid bromine, and shaken till it had been entirely absorbed. This treatment with liquid bromine was continued until a permanent red color in the solution indicated that an excess had been added, when the flask was heated on the steam bath for several hours. At the end of this time the solution with the oil below it was poured into a beaker and allowed to cool, when the oil solidified, and was easily removed. The yield of this crude product did not rise above 30 grams. The yellow crystalline solid was purified by pressing with filter paper to remove an oily impurity, followed by crystallization from naphtha, until it showed the constant melting point 97° – 98° . It was dried *in vacuo* for analysis.

¹ Different results were obtained with dilute bromine water or with pure bromine. They will be described later.

I. 0.2666 gram substance gave 0.0962 gram CO_2 and 0.0138 gram H_2O .

II. 0.3359 gram substance gave 0.1166 gram CO_2 and 0.0150 gram H_2O .

III. 0.2033 gram substance gave 0.4097 gram AgBr.

IV. 0.0810 gram substance gave 0.1637 gram AgBr.

	Calculated for $\text{C}_7\text{HBr}_7\text{O}_2$	I	II	Found	III	IV
C	9.20	9.84	9.47			
H	0.15	0.58	0.50			
Br	85.90				85.78	86.00

The substance has been determined by the reactions discussed later to be a diketone, the heptabromomethyldiacetyl $\text{CBr}_3\text{CHBrCOCOCBr}_3$.

Properties.—It crystallizes from naphtha in brilliant yellow plates shaped like an arrow head and from alcohol in diamond-shaped scales, but a slight oily impurity is formed by the action of the alcohol on the substance. It melts at $97^\circ\text{--}98^\circ$. It is easily soluble in alcohol, methyl alcohol, ether, benzene, carbonic tetrachloride, or glacial acetic acid; slightly soluble in naphtha; essentially insoluble in water. Naphtha is the best solvent for it. Fuming nitric acid, when boiling, dissolves it, and the compound seems to crystallize out unaltered, but analyses showed that it had lost between one and two per cent. of bromine. If boiled for several hours with nitric acid, complete decomposition takes place, as the solution leaves no residue on evaporation. Boiling with sulphuric acid diluted with its own volume of water gives bromoform, but in such small amount that only a very slight decomposition is indicated. Strangely enough, it is much less stable toward water than toward this dilute acid, as, if it is boiled with water for some time, it is decomposed completely into bromoform, hydrobromic acid, and oxalic acid. A solution of sodic hydroxide decomposes the diketone with the formation of bromoform. Cold sodic methyrate dissolves it, and the solution gives a test for a bromide but none for an oxalate. The principal product melted at 80° and was colorless. Unfortunately we did not have time to study it. If the sodic methyrate was

hot, the diketone was decomposed, giving bromoform, sodic bromide and sodic oxalate. The behavior of the diketone with an aqueous solution of sodic carbonate will be described in detail later. Boiling with an aqueous solution of sodic acetate converted the diacetyl into bromoform, hydrobromic acid and oxalic acid. When boiled with water containing calcic carbonate a sharp odor like that of a brom ketone was observed, but only tarry products were obtained from which no definite compound could be isolated. The same odor was produced by boiling with water containing finely divided silver, and oxalic acid and bromide of silver were formed. When the diacetyl was shaken with a mixture of aqueous ammoniac hydroxide and alcohol, a precipitate was formed, recognized as oxamide by its essential insolubility in all solvents but glacial acetic acid, its infusibility, and its decomposition by an alkali into ammonia and an oxalate. Analyses confirmed this inference. A benzene solution of the diketone treated with aniline gave a white precipitate consisting of pearly scales, which after crystallization from glacial acetic acid melted at 245° - 246° ; it was therefore oxanilide, which according to Gerhardt¹ melts at 245° . Boiling alkali converted it into aniline and an oxalate. As phenylhydrazine formed a large amount of its hydrobromide, when it acted on the diacetyl, we did not attempt to study its behavior further. Hydroxylamine hydrochloride had no apparent action on it. *o*-Phenylenediamine in benzene solution gave in time a grayish yellow precipitate, which did not melt below 275° , and was free from bromine. It was slightly soluble in the organic solvents except hot glacial acetic acid, and crystallized in very small prisms terminated by a basal plane. It contained 16.53 per cent. of nitrogen, and is therefore probably the *o*-phenylene-oxamide,² which contains 17.29 per cent. of nitrogen. Pyridine converted the diacetyl into a black tar containing a few colorless crystals. No action could be obtained with acetic anhydride, or acetyl chloride reinforced by sodic acetate, even when boiled for several hours, and the Baumann-Schotten

¹ Ann. Chem. (Liebig), **60**, 308 (1846).

² R. Meyer, Seeliger: Ber. d. chem. Ges., **39**, 2641.

process was also without action. Preliminary experiments on the reduction of the diacetyl led to no satisfactory result. Sulphurous acid apparently did not act, while zinc and acetic acid or aluminum amalgam seemed to give tars. Bromine in the cold did not seem to affect the diacetyl, and when heated with it in a sealed tube, tarry products were formed.

Decomposition of Heptabrommethyldiacetyl by Sodic Carbonate

When the diketone was allowed to stand several days with a solution of one gram of sodic carbonate in 10 grams of water, carbonic dioxide was given off, an oil collected at the bottom, and the water gave strong tests for bromide and oxalate; these seemed to be the only soluble products, as, after removing the oil, a portion of the solution was acidified with hydrochloric acid, and extracted with ether, to which it gave up nothing but a little oxalic acid. In addition to the oil, the bromide, and the oxalate there should be another product containing the fifth atom of carbon, but a careful search for formaldehyde, or formic acid, which we expected, failed to detect either, so that we are of the opinion that this atom of carbon was converted into carbonic dioxide, which escaped with that formed from the sodic carbonate; and this view is supported by the appearance of some carbonic dioxide when the diacetyl undergoes a similar decomposition on being heated to 100° with water.

The oil mentioned above was obtained in such small quantities that a determination of the boiling point in the usual way could not give a result definite enough to be of any value in identifying it. Accordingly we used the following method contrived by one of us (Fiske) for this purpose. The oil separated from the aqueous liquid was distilled with a few drops of water from a small side-neck test tube, when the boiling point was found to be 93° – 94° with the barometer at 762 mm. The vapor pressure of water at that temperature is 599 mm.,¹ and subtracting this we obtain 163 mm. as the vapor pressure of the other liquid. As from its odor we suspected that our oil was bromoform, we next found the vapor

¹ Landolt and Börnstein, 119 (1905).

pressure of bromoform at this temperature from the determinations given in the following table:

Vapor Pressures of Bromoform

Temperature	Pressure
46°	14-15 mm.
50°.6	20.8 mm.
54°.6	26.24 mm.
61°.6	37.88 mm.
68°.2	54.46 mm.
150°.5	760 mm.
151°.2	760 mm.
120°.3	330 mm.

The last two observations are given by Thorpe,¹ the others by Kahlbaum.² From these data a curve was constructed (Fig. I), which showed that the vapor pressure at 93°-94° was between 162 and 164 mm., that is, as near to an exact agree-

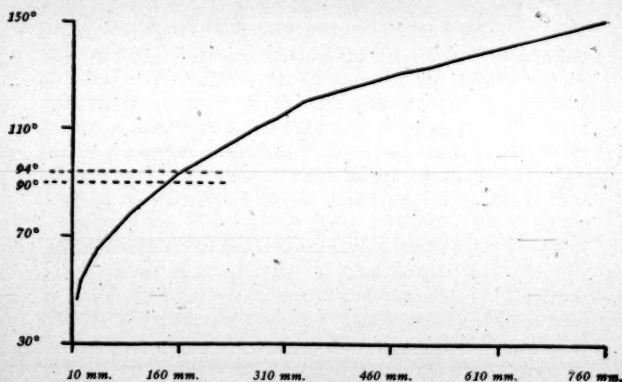


Fig. I

ment with our 163 mm. as the roughness of the method permits. The oil, which had distilled over with the water, was next dried by wiping with moist filter paper³ and analyzed.

¹ P. Chem. Soc., 87, 201.

² Siedetemperatur und Druck, 96.

³ Jackson, Fiske: *THIS JOURNAL* 44, 438 (1910).

- I. 0.2943 gram substance gave 0.6560 gram AgBr.
 II. 0.2391 gram substance gave 0.5339 gram AgBr.

	Calculated for CHBr ₃	I Found	II
Br	94.86	94.86	94.99

There can be no doubt, therefore, that the substance is bromoform.

We also determined the amounts of the three decomposition products. For this purpose a weighed portion of the diacetyl was allowed to stand with a solution of sodic carbonate until it was completely decomposed. It was then distilled until the bromoform had passed over, when the residue was acidified with acetic acid, the oxalic acid determined by precipitation with calcic nitrate, and the bromide precipitated from the filtrate with argentic nitrate after acidification with nitric acid. An approximate idea of the amount of bromoform was obtained by weighing it after separation from the distilled water. To do this it was poured into a bulb, the bottom of which had been drawn out to a sealed capillary tube; after the oil had collected, the end of the capillary was broken, and the bromoform blown out through it, thus effecting a separation from all but a fraction of a drop of the water, which was then removed by wiping with moist filter paper.

I. 0.6040 gram substance gave 0.0487 gram CaO, 0.2319 gram AgBr and 0.3524 gram CHBr₃.

II. 0.5866 gram substance gave 0.0453 gram CaO, 0.1833 gram AgBr and 0.3182 gram CHBr₃.

	Calculated for C ₂ H ₂ Br ₂ O ₄	I Found	II
H ₂ C ₂ O ₄	13.78	12.96	12.41
Br	12.26	16.28	13.30
2CHBr ₃	77.50	58.34	54.25

The percentages of oxalic acid found agree as closely as could be expected with that required by the formation of one molecule of oxalic acid. While the results for the bromine show great variations, they make it plain that only one atom of bromine was eliminated as sodic bromide. The variations are probably due to the decomposition of a larger or smaller portion of the

bromoform. This would also interfere with the accuracy of the determination of the bromoform, but is insignificant compared with the losses in distilling, collecting, and, above all, in drying this substance by wiping. In our paper¹ on this method of drying we show that about one-third of the substance is usually lost, and, if that was the case here, our results are very near to the calculated percentage for two molecules of bromoform. But it is not necessary to apply this rather doubtful correction in order to use our results, for, as they stand, they are about 20 per cent. higher than 38.75, the percentage calculated for one molecule, and since all the experimental errors in our process tend to diminish the amount of bromoform found, our results, showing that much more than one molecule was formed, indicate that the actual quantity was two molecules.

Action of Water at 100° on the Diketone.—When the diketone was heated to 100° in a sealed tube with water for several days, a white crystalline substance was the principal product of the reaction, although small quantities of bromoform and carbonic dioxide and 17 to 19 per cent. of hydrobromic acid were also observed. The main product after recrystallization from alcohol showed the constant melting point 71°–72° and was dried *in vacuo* for analysis (Analyses I–II). What seemed to be the same compound was obtained from the mother liquors of the diketone in purifying that substance. It melted at 70°, but gave the same result on analysis (IV and V).

- I. 0.1161 gram substance gave 0.2416 gram AgBr.
- II. 0.1789 gram substance gave 0.3715 gram AgBr.
- III. 0.1330 gram substance gave 0.2763 gram AgBr.
- IV. 0.1143 gram substance gave 0.2387 gram AgBr.
- V. 0.2279 gram substance gave 0.4736 gram AgBr.

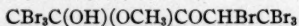
	I	II	III Found	IV	V
Br	88.53	88.37	88.39	88.88	88.43

Experiments are now in progress to settle the constitution of this substance. It crystallizes in bunches of long, thin, pale yellow needles, which turn slightly brownish on exposure to the air. It melts at 71°–72°. It is easily soluble in alcohol,

¹ THIS JOURNAL, 44, 438 (1910).

methyl alcohol, ether, chloroform, tetrachloride of carbon, acetone, ethyl acetate, glacial acetic acid, or benzene, fairly soluble in ligroin, essentially insoluble in water. The best solvent for it is hot alcohol. The substance is tolerably stable, as standing for two days with cold alcohol left it unchanged, and the same was true of acetic anhydride in the cold. Analysis III was made with a specimen which had undergone this treatment. If boiled with acetic anhydride, an uncrystallizable oil was formed.

Heptabrommethyldiacetyl Monomethyl Hemiacetal,



The diketone dissolved in absolute methyl alcohol was allowed to stand at ordinary temperatures for two days, and the solvent was then allowed to evaporate spontaneously, when colorless prisms were obtained. These were recrystallized from methyl alcohol until they showed the constant melting point 100° – 101° when they were dried *in vacuo*.

I. 0.3053 gram substance gave 0.1178 gram CO_2 and 0.0265 gram H_2O .

II. 0.1436 gram substance gave 0.2746 gram AgBr.

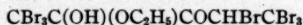
III. 0.2177 gram substance gave 0.4160 gram AgBr.

	Calculated for $\text{C}_8\text{H}_5\text{Br}_7\text{O}_5$	I	Found II	III
C	10.51	10.52		
H	0.73	0.97		
Br	81.75		81.21	81.32

Properties of Heptabrommethyldiacetyl Monomethyl Hemiacetal.—It crystallizes from methyl alcohol in colorless prisms, which melt at 100° – 101° , and tend to turn brown when exposed to the air, especially if moist. It is easily soluble in alcohol, methyl alcohol, chloroform, tetrachloride of carbon, acetone, ethyl acetate, or benzene, less soluble in ligroin; essentially insoluble in water. When boiled with sulphuric acid diluted with its own volume of water, it was converted into an oil, and gave off an odor like camphor. It dissolved partially in strong nitric acid but apparently without decomposition, as the solution gave no test for bromine. Alcoholic

ammonia formed ammoniac bromide. Aniline gave an oil. Hydroxylamine hydrochloride, acetic anhydride, or acetyl chloride did not act upon it. A methyl alcohol solution boiled for some time with finely divided silver gave an oil which, on standing, deposited white crystals melting at about 70° , but we have not had time to study them.

Heptabrommethyl diacetyl Monoethyl Hemiacetal,



The diketone allowed to stand with alcohol for two days deposited large masses of colorless crystals, which were recrystallized from alcohol until they showed the constant melting point 93° – 94° , when they were dried *in vacuo*.

I. 0.2257 gram substance gave 0.1016 gram CO_2 and 0.0255 gram H_2O .

II. 0.1661 gram substance gave 0.3129 gram AgBr.

III. 0.1849 gram substance gave 0.3464 gram AgBr.

	Calculated for $\text{C}_8\text{H}_7\text{Br}_7\text{O}_5\text{C}_2\text{H}_5\text{OH}$	I	Found II	III
C	12.01	12.35		
H	1.00	1.25		
Br	80.11		80.17	79.75

Properties of Heptabrommethyl diacetyl Monoethyl Hemiacetal.

—It crystallizes from hot alcohol in irregular masses of flat angular plates forming serrated ridges, which are white but easily turn brown when moistened with the solvent and exposed to the air. Specimens which had undergone this change were found on analysis to give amounts of bromine which were about 2 per cent. too low. It melts at 93° – 94° . It was easily soluble in alcohol, methyl alcohol, ether, acetone, or ethyl acetate; soluble in benzene, chloroform, tetrachloride of carbon, or glacial acetic acid; slightly soluble in ligroin; essentially insoluble in water.

When a specimen of the ethyl hemiacetal was heated with a few cc. of water to 100° for several days, upon opening the tube a little carbonic dioxide escaped, and there was left an oil and an aqueous liquid. The oil smelled of bromoform, but after this had been allowed to evaporate, the residue was still oily, with a bitter ethereal odor, and contained a few crystals of the

unaltered hemiacetal. These were removed, and the oil on distillation was found to boil between 183° and 193° , but owing to the small amount of substance no more accurate determination could be made. It is probably therefore the diethyl oxalic ester which boils at 186° according to Weger,¹ and can be formed by distillation from the monoethyl ester,² the secondary products being ethyl formic ester and carbonic dioxide. This inference was confirmed by a determination of the quantity of oxalic acid in the water solution, which amounted to less than 1 per cent. No formic acid could be detected in the products of the reaction, but much hydrobromic acid was formed.

Sodic carbonate in aqueous solution decomposed the hemiacetal in the same way that it did the diketone, but a quantitative study of this reaction gave less satisfactory results. The amount of bromoform was over 10 per cent. above that required by one molecule; the bromine agreed fairly with the amount for one atom, but the oxalic acid was only about half the percentage required by one molecule. This experiment therefore confirms the one tried with the diketone itself, the deficiency in oxalic acid being accounted for by the formation of oxalic ester.

Hydroxylamine hydrochloride or cold acetic anhydride had no action on the monoethyl hemiacetal; hot acetic anhydride converted it into an uncrystallizable oil. When the diketone was heated with alcohol a more deep-seated reaction took place than in the cold, giving tarry products with an odor like that of a brom ketone.

Action of other Alcohols on Heptabrommethyldiacetyl

When this diketone was allowed to stand with amyl alcohol for several days, and then freed from the alcohol by a blast of air, a yellow oil was obtained, which we did not succeed in bringing to crystallization. To our great surprise an analysis gave a percentage of bromine agreeing with that in the hemiacetal.

¹ Ann. Chem. (Liebig), **221**, 87 (1884).

² Anschütz: Ber. d. chem. Ges., **16**, 2413 (1883).

0.2433 gram substance gave 0.4291 gram AgBr.

	Calculated for $C_8HBr_7O_2C_8H_{11}OH$	Found
Br	75.58	75.06

Similar treatment of the diketone with benzyl alcohol gave a solid product which crystallized from hot alcohol in large, colorless crystals showing the constant melting point 104° – 105° , but the analyses proved the substance was not the expected hemiacetal, as we found C 22.58, H 1.90, Br 67.89, 68.29, 67.90, and $C_8HBr_7O_2C_7H_7OH$ requires C 18.92, H 1.16, Br 73.55. We have not succeeded in finding, for this substance, any formula which could be derived simply from those of its constituents, so that its nature must be left unexplained until more work can be done on it.

Action of Bromine on a Dilute Solution of the Tribromcarboxylketocyclopentene Ether of Oxalhydroxyacetic Acid

As already stated, bromine acting on a strong solution of the acid melting at 207° converts it into the heptabrommethyl-diacetyl melting at 97° – 98° , but if a dilute solution of the acid was treated with bromine in the cold, a precipitate was formed which was white instead of yellow, much less carbonic dioxide was given off, and a little of an oil was obtained, identified as bromoform by its smell and its vapor pressure when distilled with water according to the method already described. The colorless precipitate was crystallized from ligroin, until it showed the constant melting point 96° – 97° . It is strange that this is so near to that of the diacetyl, 97° – 98° . That it was a different substance is shown not only by the following analyses, but by its white color and behavior with sodic carbonate. The substance was dried *in vacuo*.

I. 0.2903 gram substance gave 0.1299 gram CO_2 and 0.0395 gram H_2O .

II. 0.2421 gram substance gave 0.1079 gram CO_2 and 0.0285 gram H_2O .

III. 0.2166 gram substance gave 0.4038 gram AgBr.

IV. 0.1899 gram substance gave 0.3536 gram AgBr.

	Calculated for $C_7H_5BrO_4$	I	II	Found	III	IV
C	12.05	12.21	12.15			
H	0.72	1.17	1.31			
Br	80.35			79.34	79.21	

These results agree fairly with those calculated for $CBr_3COCH(OCH_2CHO)CHBrCBr_3$, and as this substance would be expected from the method of preparation, we assign this constitution to it provisionally. Attention should also be drawn to the fact that this formula has essentially the same percentage composition as the heptabrommethyldiacetyl monoethyl hemiacetal $CBr_3C(OHOC_2H_5)COCHBrCBr_3$, as they differ only by 2 atoms of hydrogen. In many of their properties the two substances resemble each other, but this compound cannot be the hemiacetal, because no alcohol was used in its preparation, and also since it behaves in an entirely different way with sodic carbonate.

Properties of the Heptabromketosecondaryamyl Ether of Glycolaldehyde.—It crystallizes from alcohol in short, thick, white prisms, which show a tendency to turn brown on exposure to the air. It melts at $96^\circ-97^\circ$. It is easily soluble in alcohol, methyl alcohol, or benzene, but each of these solvents converts it partially into a sticky liquid. Ligroin, in which it is less soluble, is the best solvent for it.

When this compound was allowed to stand with a solution of sodic carbonate, only a trace of bromoform was obtained, the product being a voluminous precipitate of white crystals, while bromide, but no oxalate, was detected in the aqueous liquid. The precipitate was recrystallized from ligroin, until it showed the constant melting point $71^\circ-72^\circ$, when it was dried *in vacuo*.

I. 0.1550 gram substance gave 0.2758 gram AgBr.

II. 0.1303 gram substance gave 0.2322 gram AgBr.

	Calculated for $C_7H_5BrO_4$	I	Found	II
Br	75.70	75.73	75.86	

This compound, therefore, is formed by the replacement of one atom of bromine by hydroxyl in the preceding substance

and its provisional formula is $\text{CBr}_3\text{COCH}(\text{OCH}_2\text{CHO})\text{CH}(\text{OH})\text{CBr}_3$. It is unfortunate that the importance of these compounds was not appreciated until it was too late to settle their constitution definitely by further work.

Properties of the Hexabromketohydroxysecondaryamyl Ether of Glycolaldehyde.—It forms white crystals melting at $71^\circ\text{--}72^\circ$, which are soluble in most of the organic solvents, except ligroin. In this it is soluble only when hot; insoluble in water.

When the dry acid melting at 207° was treated with dry bromine, no action could be detected, but on adding water the effervescence accompanying the formation of the diacetyl at once set in.

The Acid Melting at 121°

This substance was obtained occasionally from the benzene mother liquors left after the tribromcarboxylketocyclopentene ether of oxalhydroxyacetic acid (melting at 207°) had crystallized out, when they were allowed to stand in an open dish for some days. The new acid was deposited in large masses of colorless crystals, which were purified by recrystallization from benzene, until they showed the constant melting point 121° . They were dried *in vacuo*.

I. 0.3717 gram substance gave 0.5483 gram AgBr.

II. 0.2680 gram substance gave 0.3950 gram AgBr.

	Calculated for $\text{C}_{10}\text{H}_5\text{Br}_2\text{O}_7$	I	Found	II
Br	62.81	62.76		62.72

It crystallizes from glacial acetic acid or benzene in white rhombic prisms, which melt at 121° with effervescence, leaving a residue which does not melt below 250° . The gas given off, which fumes in moist air and smells like hydrobromic acid, was identified as that body by passing it into water, when on addition of nitric acid and argentic nitrate it gave a yellowish white precipitate. It contains no carbonic dioxide, since it gave no precipitate with lime water. The acid is easily soluble in water, and in all the organic solvents except ligroin. Its aqueous solution set free carbonic dioxide from calcic carbonate. As the time at our disposal did not allow a fuller

study of this substance it is not worth while to try to assign a formula and name to it.

The Acid Melting at 174°. Dibromhydroxycarboxylcyclopentene Orthodiether of Carboxyldihydroxyisocrotonlactone

This compound was prepared by dissolving 200 grams of sodic hydroxide in a liter of water, and adding to this solution, which had been cooled in an ice chest, 100 grams of tetrabrom-orthoquinone in small portions at a time with constant shaking. After standing for several hours to make sure that the reaction had run to an end, the liquid was poured into a large beaker containing 300 cc. of strong hydrochloric acid, which neutralized the alkali, and precipitated a sticky yellowish brown substance, and this after standing overnight was filtered out, and the filtrate extracted repeatedly with ether.¹ The residue left after the ether had evaporated spontaneously was not impregnated with oil, as in the preparation of the acid melting at 207°, and therefore was extracted with successive portions of hot benzene and then recrystallized either from this solvent, or from glacial acetic acid, until it showed the constant melting point 174°.

I. 0.2588 gram substance gave 0.2871 gram CO₂ and 0.0508 gram H₂O.

II. 0.2812 gram substance gave 0.3124 gram CO₂ and 0.0593 gram H₂O.

III. 0.2241 gram substance gave 0.1898 gram AgBr.

IV. 0.2594 gram substance gave 0.2194 gram AgBr.

	Calculated for C ₁₀ H ₈ Br ₂ O ₄	I	II	Found	III	IV
C	29.64	30.26	30.28			
H	1.36	2.19	2.88			
Br	36.20				36.06	35.99

Properties of Dibromhydroxycarboxylcyclopentene Orthodiether of Carboxyldihydroxyisocrotonlactone.—It separates from ether in pale yellow, round grains, which are very pulverulent when dry. It melts at 174° with decomposition; and is easily soluble in water, alcohol, methyl alcohol, ether, acetone, glacial

¹ The extraction was most economically carried on in the apparatus invented by one of us (Fiske), *THIS JOURNAL*, 41, 510 (1909).

acetic acid, ethyl acetate, or benzene; slightly soluble in chloroform, or tetrachloride of carbon; essentially insoluble in naphtha. The best solvent for it is glacial acetic acid, in which it is much more soluble hot than cold. The aqueous solution gives an acid reaction with litmus paper, and decomposes carbonates with evolution of carbonic dioxide.

The basicity of the acid was determined by titration with a fifth-normal solution of potassic hydroxide, phenolphthalein being used as the indicator.

- I. 0.1945 gram substance required 7.54 cc. of the solution.
 II. 0.2793 gram substance required 10.35 cc.

	Calculated for $C_{11}H_5Br_7O_9K_3$	I Found	II
K	21.09	23.27	22.46

The acid is therefore tribasic, but we did not succeed in preparing salts of it in a state fit for analysis. Our attempt which approached most nearly to success consisted in treating a strong aqueous solution of the acid with baric carbonate, and, after warming to drive off the excess of carbonic dioxide, filtering and evaporating to dryness. The filtrate turned brown, as it evaporated, but in spite of this two determinations of barium were made, which gave 21.61 and 21.38 per cent. of Ba instead of 23.73, the amount in $BaH_4C_{11}Br_7O_9$. The water of crystallization also came out 1 per cent. below that required for one molecule. Attempts to avoid the decomposition of the salt by working in the cold gave discordant results, owing to the dissolved baric carbonate. An attempt to make the ammonium salt gave a brown solution containing ammonic bromide. A solution of the calcium salt made from the acid and calcic carbonate gave brown precipitates with argentic nitrate, mercurous nitrate, or plumbic acetate. When the acid melting at 174° was treated with bromine and water, it gave the heptabrommethylidiacetyl, $CBr_3CHBrCOCOCBr_3$, also obtained from the acid melting at 207° ; in fact, our principal supply of this diketone was obtained from this acid. The amount of carbonic dioxide given off during the action of bromine and water on the acid was determined as follows:

- I. 0.1945 gram substance yielded 0.2580 gram BaCO_3 .
 II. 0.2793 gram substance yielded 0.3943 gram BaCO_3 .

	Calculated for 3 molecules of CO_2	I	Found II
CO_2	29.80	29.63	31.53

It therefore also gives off three molecules of carbonic dioxide like the acid melting at 207° , under which the details of the method of determination will be found. The diketone was identified by its melting point, 97° – 98° , its bright yellow color, and arrow-head crystals. When the action of bromine on a more dilute solution of the acid melting at 174° was tried, none of the colorless substance melting at 96° – 97° was formed, which was obtained under the same conditions from the acid melting at 207° , but the product was the yellow diketone. The reactions also differed in the fact that no bromoform was produced in this case.

The Acid Melting at 217°

Tetrabromorthoquinone was shaken for 10 minutes with a normal solution of sodic hydroxide cooled to 6° . At the end of this time the green color, which appeared at first, had disappeared, and the liquid was acidified with hydrochloric acid, and after filtering out the precipitate of tetrabrompyrocatechin extracted with ether. Upon evaporating off the ether a crystalline solid impregnated with a yellow oil was obtained, which was pressed on a porous plate to remove the oil, and then crystallized from hot benzene until it showed the constant melting point 217° , when it was dried *in vacuo*.

- I. 0.2011 gram substance gave 0.2525 gram AgBr .
 II. 0.2288 gram substance gave 0.2895 gram AgBr .

	Calculated for $\text{C}_{10}\text{H}_4\text{Br}_4\text{O}_2$	I	Found II
Br	54.23	53.43	53.81

Properties.—It crystallizes in shining yellowish white prisms, which melt at 217° with decomposition. It is easily soluble in all the common organic solvents except benzene and ligroin. In benzene it is slightly soluble in the cold, soluble when hot; in ligroin it is almost insoluble; soluble in water. Benzene is

the best solvent for it. It has a strong acid reaction and its aqueous solution decomposes calcic carbonate.

The salts are far from stable, potassic carbonate, for example, giving a reddish solution with the acid, and the calcium salt turning brown when its solution is evaporated. In spite of this, however, we obtained a calcium determination which agrees well with the analyses for bromine given above.

The calcium salt was prepared by the action of a strong aqueous solution of the acid on an excess of calcic carbonate; the aqueous solution was boiled to drive off carbonic dioxide, filtered, and the filtrate evaporated to dryness.

I. 0.2428 gram of the air-dried salt lost 0.0361 gram on heating to 110° .

II. 0.2074 gram substance gave 0.0467 gram CaSO_4

	Calculated for $\text{C}_{10}\text{H}_4\text{Br}_7\text{O}_7\text{Ca} \cdot 6\text{H}_2\text{O}$	Found
H_2O	14.68	14.86
	Calculated for $\text{C}_{10}\text{H}_4\text{Br}_7\text{O}_7\text{Ca}$	Found
Ca	6.37	6.62

Although this determination agrees with our analyses for bromine, we feel that more experimental work is necessary before the formula given above can be considered definitely established.

The solution of the calcium salt gave a black precipitate with argentic nitrate, or mercurous nitrate, a dark brown precipitate with plumbic acetate, or ferric chloride, a yellow precipitate with baric chloride, no precipitate with mercuric chloride, or cobaltous nitrate. We are unable to determine whether the colors of these precipitates belonged to the salts, or were caused by the decomposition observed during the boiling off of the carbonic dioxide in making the calcium salt.

When treated with bromine and water, the acid melting at 217° did not give the heptabrommethylidiacetyl melting at 97° – 98° obtained from the acids melting at 207° and 174° . Instead of this, white needles were formed melting at 156° , and showing a tendency to turn brown on exposure to the air. Unfortunately the time at our disposal did not permit us to

make a further study of this promising substance, or of the other properties of the acid melting at 217° .

The Oily Product

By the action of the weaker solutions of sodid hydroxide on tetrabromorthoquinone an oily product was obtained in addition to the solid acid melting at 207° or 217° , but none of this was formed with the stronger lye which gave the acid melting at 174° . In the introduction we have shown that certain inferences in regard to the nature of the oil can be drawn from our quantitative experiments, the details of which follow. A fifth-normal solution of potassic¹ hydroxide was used, therefore much more dilute than those which had yielded our definite acids. The amount of alkali used was determined by mixing an excess of it with a weighed quantity of powdered tetrabromorthoquinone, and allowing the mixture to stand in a corked flask until the reaction was complete, when the excess of alkali was determined by titration with one-fifth normal hydrochloric acid, phenolphthalein being used as the indicator. The carbonic dioxide formed was collected in a solution of baric hydroxide, the whole being set free by a large excess of hydrochloric acid and heat. The bromine removed was determined by another experiment, in which the quinone was decomposed by potassic hydroxide free from halogen, and the solution precipitated with argentic nitrate after acidification with nitric acid. The argentic bromide was freed from organic matter by treatment with a large amount of alcohol, followed by hot nitric acid, and finally by washing again with water and alcohol.

I. 0.3482 gram $C_6Br_4O_2$ used 14.12 cc. KOH solution and gave 0.0607 gram $BaCO_3$.

II. 0.4538 gram $C_6Br_4O_2$ used 17.52 cc. KOH solution and gave 0.0554 gram $BaCO_3$.

III. 0.4549 gram $C_6Br_4O_2$ used 17.78 cc. KOH solution and gave 0.0561 gram $BaCO_3$.

IV. 0.4234 gram $C_6Br_4O_2$ gave 0.3841 gram AgBr.

V. 0.3866 gram $C_6Br_4O_2$ gave 0.3504 gram AgBr.

¹ Potassic hydroxide apparently acts like sodid hydroxide.

	Found for each molecule $C_6Br_4O_2$				
	I	II	III	IV	V
KOH	192.9	183.7	186.0		
CO ₂	16.47	11.53	11.65		
KBr				243.7	243.5

The results are given in units of molecular weight, and agree even more closely than we expected.

THE BEHAVIOR OF TETRABROMORTHOQUINONE WITH ALKALINE REAGENTS OTHER THAN SODIC HYDROXIDE

As stated earlier in this paper an aqueous solution of sodic hydroxide converted the tetrabromorthoquinone into a green substance which disappeared after the reagents had been shaken together for 10 or more minutes. The aqueous liquid thus obtained gave, on acidification, tetrabrompyrocatechin, and on extracting the filtrate from this with ether one or more of the acids already described. In the hope of tracing the limits of the reaction experiments were tried in which the nature of the alkaline substance was varied; and these showed that potassic hydroxide or ammoniac hydroxide gave results apparently similar in every way to those obtained with sodic hydroxide, and therefore they were not studied in detail. A half-normal solution of baric hydroxide after standing for several days in the cold gave a green product, which at the end of 10 days had changed into yellowish feathery crystals showing no test for a carbonate. When these were washed with water, a solution with the strong purple color of sodic bromanilate was formed, and the solid became tarry. The filtrate from the crystals yielded on acidification no precipitate of tetrabrompyrocatechin, but this was to be expected, for a special experiment showed that the pale yellow barium salt of tetrabrompyrocatechin is insoluble. The acidified filtrate gave up to ether a yellow acid melting at 202° , when not perfectly pure, and therefore undoubtedly the acid melting at 207° . Plumbic hydroxide had no perceptible action on tetrabromorthoquinone.

A normal solution of sodic carbonate acted on tetrabromorthoquinone in the same way as sodic hydroxide, except that the solution was redder, the precipitate on acidification scanty

and more tarry, and bromanilic acid was detected in addition to the acid melting at 217° . A normal solution of acid sodic carbonate in the cold gave none of the green compound but a chocolate-brown solid and much bromanilic acid, whereas, if the aqueous solution acted on a solution of the quinone in benzene, a greenish precipitate was formed and the solution (which was not colored by bromanilic acid) upon treatment with bromine and water gave colorless needles melting at 94° - 95° , when not perfectly pure, and which were therefore probably the heptabromketosecondaryamyl ether of glycolaldehyde, which is colorless and melts at 96° - 97° . The formation of this ether would indicate that the acid melting at 207° had been formed.

The effect of heat on the reaction was also studied. If a fifth-normal sodic hydroxide solution was warmed on the water bath with tetrabromorthoquinone for two minutes, no green product was formed, the red quinone being directly converted into a chocolate-brown substance, which after an hour on the steam bath had become dull red. Upon washing this solid with alcohol the red ether $C_6Br_4O_2C_6Br_2O_2$ was obtained in quantities of about 1 gram from five of the quinone. The appearance of the ether can be explained on the supposition that the boiling was not long continued enough to decompose it completely. The dark-colored solutions contained the other products of the reaction, of which we can give no account except that we did not succeed in detecting tetrabrompyrocatechin or bromanilic acid in them. The red ether $C_6Br_4O_2C_6Br_2O_2$ was also obtained by boiling the quinone with a solution of sodic carbonate, or of baric hydroxide, but the presence of the alkaline reagent is not necessary for the formation of the ether, as, when the tetrabromorthoquinone was boiled with water alone for half an hour, about one-fifth of it was converted into this ether. This result confirms the similar observation of Porter and one of us.¹ The same change seemed to take place very slowly in the cold.

In order to determine the source of the bromanilic acid observed in several of these experiments we studied the be-

¹ THIS JOURNAL, **31**, 119 (1904); also **33**, 173 (1907).

havior of tetrabromopyrocatechin and of the hexabromorthoquinopyrocatechin ether with sodic hydroxide. By the action for 5 hours of a boiling twice-normal solution of sodic hydroxide a considerable amount of tetrabromopyrocatechin was converted into bromanilic acid, recognized by the deep purple color of its sodium salt; but in the cold the reaction did not take place even with this concentrated solution, and with more dilute alkaline solutions bromanilic acid could not be obtained even at the boiling point.

The red ether $C_6Br_4O_2C_6Br_2O_2$, after standing in the cold for two days with a twice-normal solution of sodic hydroxide, gave a quantity of the black precipitate observed by Koch and one of us,¹ which was identified as sodic bromanilate, while some of it colored the solution purple-red. Acidification of the liquid gave a copious precipitate of tetrabromopyrocatechin, but none of our acids could be obtained from the filtrate, which gave up to ether nothing but a little bromanilic acid.

CAMBRIDGE, September 19, 1913

THE VISCOSITY OF UNDERCOOLED WATER AS MEASURED IN A NEW VISCOSIMETER

BY GEORGE F. WHITE AND RALPH H. TWINING

While there is at hand² a great variety of information concerning the change of many properties of substances in the region of their melting point, very little attention has been devoted to a study of the viscosity changes. The discontinuity of the viscosity curves of a few crystalline liquids at their melting point has been indicated by the work of Schenck,³ and further investigation along this line should furnish results of considerable value. Tammann⁴ regarded viscosity as an important criterion of the passage of a liquid into the crystalline condition, but observed that there is no "break" in

¹ THIS JOURNAL, **36**, 10 (1901).

² Very recently [Gazz. chim. ital., **43**, II, 281 (1913)], Nasini and Bresciani have undertaken an investigation on the discontinuity phenomena at the melting point. This will be referred to in a later article.

³ Z. physik. Chem., **27**, 167 (1898).

⁴ *Ibid.*, **28**, 17 (1899).

the viscosity curves of liquids passing into the amorphous state. Amorphous substances could be considered as undercooled liquids. His investigations were not carried out at the melting point, but far below this temperature, where the viscosity of the undercooled liquid is enormously high and where there is a maximum in the number of nuclei which appear in a definite interval of time. At these temperatures no irregularities in the viscosity curves were observed.

The change in the rate of crystallization of a liquid on undercooling has been ascribed to many causes. Different investigators have stated that it is due to differences in the disposition of the crystals in their formation, to impurities in the liquid, to slow conduction of heat from the surface of crystallization, and may be influenced by the shape of the containing vessel. Wilson¹ considered the older explanations for the increase in velocity of solidification of undercooled liquids to a maximum as the temperature was lowered to be very unsatisfactory or incomplete. He supposed that it was a function of the viscosity, and deduced the relation $v = Ct/\eta$ where v is the velocity of crystallization, C a constant dependent on the nature of the liquid, t the degrees of undercooling, and η the viscosity. The temperature of the liquid in some cases was reduced to that at the surface of crystallization, which was at a higher temperature because of the latent heat of solidification. The velocities of crystallization as calculated agreed very well with those observed, and Wilson's assumption of a fundamental relation between viscosity and crystallization was well founded. His viscosity measurements were made by use of an Ostwald viscosimeter, and with more exact methods there is a possibility of developing a more rigid relationship.

In this preliminary paper there is presented a method for the measurement of the viscosity of liquids which eliminates many of the possibilities of error known up to this time, has practical application to the exceptionally viscous undercooled liquids and overcomes the difficulties attendant on working with them. After the collection of some necessary data on

¹ Phil Mag., [5] 60, 238 (1900).

this subject, a study of the relation between the viscosity and crystallization velocity will be made, both for pure liquids and for solutions.

The extent to which a liquid may be undercooled depends largely on its power of spontaneous crystallization, and this power is peculiarly sensitive to conditions not fully understood. As Tammann¹ has pointed out, there is a change in this property with every recrystallization of betol. Admixture of substances of varying composition shows a very different influence. Thus betol could be undercooled about 20° with the addition of 0.5 per cent. naphthalene or 0.1 per cent. salicylic acid without the appearance of any nuclei within two minutes' exposure at that temperature. On the other hand, crystallization commenced above this temperature with an admixture of 0.1 per cent. succinic acid or 5 per cent. benzamide. Insoluble substances were shown to have a great effect. In one experiment at 30° in pure betol there appeared one nucleus in two minutes, whereas no crystals were observed in a mixture of betol and 0.5 per cent. powdered glass in the same time even on cooling to -10°.

Tammann proved that the volume of liquid has considerable influence on the number of nuclei formed, but, as would be expected, there was little effect on the temperature at which crystallization commenced. The intensity of light and the magnetic field were further shown to produce no change in the phenomena of crystallization.

Tammann studied the properties of about 140 undercooled liquids and found that these could be grouped roughly into four classes according to their power to be undercooled. In the first class he placed those substances which, in passing from the fusion bath, kept 10° above the melting point, to the undercooling bath crystallized practically instantaneously. In the fourth class were those substances which could be cooled through the region where there is a maximum in the number of nuclei, and correspondingly in crystallization velocity, without the appearance of any crystallization, to a temperature where the velocity is low. No rigid rules could be adopted

¹ *Z. physik. Chem.*, **25**, 439 (1898).

concerning the relation of the property of undercooling to the nature of the substance. Hydrocarbons, alcohols, aliphatic acids and dicarboxyl acids in general may be undercooled little or not at all. Halogen and nitro derivatives of the hydrocarbons, polyatomic alcohols, hydroxy acids, aldehyde alcohols, keto acids, alkaloids and glucosides may be more or less undercooled.

Water may be undercooled very little, especially if kept in motion, without spontaneously crystallizing. We have, however, commenced our study of the viscosity of undercooled liquids with this substance in order to test the accuracy of the apparatus used, and because we consider it particularly important to establish the exact viscosity-temperature curve in the region of its melting point.

EXPERIMENTAL

Probably the most convenient form of an accurate viscosimeter which depends for the measurement of viscosity only on the physical constants of the instrument itself, and eliminates the well-known errors of the Ostwald type, is that of Bingham and White.¹ In experimenting with undercooled liquids, however, especially those which, like water, expand on solidifying and accordingly are apt to break the viscosimeter, an instrument should be used which can be most quickly constructed and calibrated. That devised by one of us² was utilized in a modified form in the present work. It lessens the possibility of introducing glass powder, dust, or other extraneous matter into the liquid. It can be made and calibrated in a few hours, and its accuracy will be shown by comparison with the results of others.

The Poisseuille formula

$$\eta = \frac{\pi r^4 p t}{8 v l} - \frac{v d}{8 \pi t l}$$

was used for the calculation of the viscosity data. η is the viscosity, r the radius and l the length of the capillary tube, d the density of the liquid, v the volume of liquid passing through the capillary, p the pressure, and t the time of flow.

¹ Z. physik. Chem., **80**, 670 (1912).

² Biochem. Z., **37**, 482 (1911).

The viscosimeter is shown in Fig. 1, and was thus constructed in order to measure the viscosity of a liquid, through great ranges in this property, in one and the same instrument. In

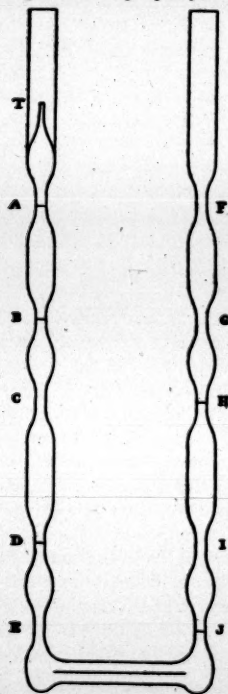


Fig. 1

working with water from 25° down to 0° C., the total volume of liquid in the viscosimeter was that between the marks *J* and *T*, and at each temperature the liquid was forced down to the mark *J*, whereby it overflowed into the trap at *T*. The volume *v*, which is that amount of liquid passing through the capillary in the time *t*, was that between the marks *A* and *D*, this volume being determined before fusing the capillary tube onto the two limbs by taking the weight of water filling this volume and reducing it to standard conditions. Volume *AD* was found to be 7.3430 cc. Viscosity determinations were always made in duplicate by taking first the time of descent of the liquid from *A* to *D* and, second, the time of ascent from *D* to *A* with the pressure reversed. This procedure¹ avoids determining the volume of the right limb and its pressure correction, as was necessary in the original form of the instrument.² The viscosimeter was then standardized with water at 25°.

$v/8\pi l$ was calculated from the known value of *v*, and an approximate value of *l* (8.3 cm.). Since this kinetic energy correction is very small, no error was introduced by a compara-

¹ Cf. Bingham and White: *Z. physik. Chem.*, **80**, 670 (1912).

² *Loc. cit.*

tively large deviation in the value of l . Taking Thorpe and Rodger's¹ value of η at 25° (0.00895), and determining p and t , from the mean of the results of four determinations the constant $\pi r^4/8l$ was calculated to be 1202×10^9 . (The approximate diameter of the capillary was 0.1 mm.)

The viscosimeter was made as nearly symmetrical as possible, but as the bulbs horizontally opposite each other in the two limbs under any conditions would differ slightly in volume and in height above the capillary tube, and also the volume of TA might differ from that of IJ , the pressure as read in the manometer did not represent the true pressure on the liquid during its passage through the capillary. The correction of the pressure, caused by the difference in height of the center of gravity of the liquid in the volumes AD and FI , is the same, though opposite in sign, according to whether the reading is taken when the liquid descends or rises in AD . Since pt is a constant, this correction may be readily calculated.

At 25° , under a pressure of about 130 cm. of water at 20° , it took about 415 seconds for the volume AD of water to pass through the capillary. At 0° under the same conditions, the time was approximately 815 seconds. Since the viscosity increases very considerably below this temperature, the time for any one determination would correspondingly increase. The time for the determination of the viscosity of an undercooled liquid should be as brief as is consistent with a low kinetic energy correction, so that it may be completed before any possible crystallization. For temperatures below 0° , therefore, the volume v was AB (2.8080 cc.), and the viscosimeter was filled between the mark H and the top of the trap T . The time of measurement, that is, the time required for the liquid to pass up or down between A and B , was reduced to about 315 seconds at 0° and the above pressure. That concordant results were obtained by using the different volumes is proven by the fact that $\pi r^4/8l$ calculated from determinations with volume AB (η being taken from data obtained by the use of volume AD) gave as a result 1201×10^9 , whereas the same value determined at 25° with volume AD gave 1202×10^9 .

¹ Phil. Trans. Lond., (A) 188, 449 (1894).

Of course the correction of the pressure was determined anew for the different "working volume" *HT*.

By the above principle of varying volumes, liquids of very different viscosities can be used in the same instrument. η^4/l being determined, the chance of error in standardizing an instrument with a shorter capillary tube by means of a liquid of high viscosity is avoided. With liquids of the ordinary viscosity it is necessary to use only one as a standard, and the careful measurement of the viscosity of water at temperatures from 0° to 100° by many investigators gives this substance the preference. A viscosimeter, capable of wider application than the one constructed, could be made having three values for v , possibly 1 cc., 2 cc., and 7 cc., if a capillary tube of the dimensions described in this article were used. Three "working volumes" would be required for such an instrument, with six bulbs in each limb, and four etchings on the left and three on the right limb. By giving the bulbs an elliptical shape the viscosimeter could be much shortened.

The arrangement of the entire apparatus, manometer, air reservoir, pressure regulator, bath and stirrer, has been previously illustrated and described.¹ For standardizing the viscosimeter at $25^\circ.00$ ($\pm 0^\circ.008$), the bath was heated by an electric globe with a toluene regulator. For temperatures below 0° the viscosimeter was immersed in ice and sodium chloride mixtures contained in a large glass jar and well stirred.

The thermometer was calibrated and standardized at the Bureau of Standards, Washington, D. C., and read from -30° to $+20^\circ$ C. It was graduated in tenths of a degree. For calibration, a Reichsanstalt thermometer reading directly to hundredths of a degree was used.

The time was read by a stop-watch reading directly to 0.2 second.

Great care was exercised to obtain a sample of water free from dust, grease and dissolved matter. Ordinary distilled water was distilled once from a chromic acid solution, and finally redistilled from a barium hydroxide solution. It was

¹ Biochem. Z., 37, 484 (1911).

preserved in Jena glass vessels which had been washed out with hydrochloric acid and the above redistilled water.

Table I

	Temp.	Viscosity	Av.
U	20°.00	0.01001	0.01003
D	20°.00	0.01004	
U	15°.00	0.01138	0.01139
D	15°.00	0.01140	
U	10°.00	0.01307	0.01307
D	10°.00	0.01306	
U	5°.00	0.01522	0.01523
D	5°.00	0.01523	
U	0°.00	0.01798	0.01798
D	0°.00	0.01798	
U	-2°.10	0.01932	0.01930
D	-2°.10	0.01928	
U	-4°.70	0.02124	0.02121
D	-4°.70	0.02117	
U	-6°.20	0.02252	0.02250
D	-6°.20	0.02247	
U	-7°.23	0.02343	0.02341
D	-7°.23	0.02338	
U	-8°.48	0.02455	0.02458
D	-8°.48	0.02461	
U	-9°.30	0.02552	0.02549
D	-9°.30	0.02546	

The viscosimeter was thoroughly cleaned by the use of fuming nitric acid. The acid was washed out with water and in some preliminary experiments this washing was followed by redistilled alcohol and redistilled ether. A current of warm air filtered through cotton wool was then drawn through the instrument to remove all the ether. By this treatment, however, water could not be undercooled in the viscosimeter below -6° without crystallizing. This was very probably occasioned by dust particles still present in the filtered air which passed through or to some minute quantity of non-volatile substance dissolved in the ether. To avoid drying with air and the use of ether, after washing with nitric acid

Table II

Temp.	Goodwin and Malley	Poiseuille	Sprung	Slotte	Thorpe and Rodger	Hosking	Bingham and White	White and Twining
0°	0.01797	0.01716	0.01778	0.01808	0.01780	0.01793	0.01797	0.01798
5°		0.01515	0.01510	0.01524	0.01512	0.01522	0.01525	0.01523
10°		0.01309	0.01301	0.01314	0.01305	0.01311	0.01301	0.01307
15°		0.01146	0.01135	0.01144	0.01137	0.01142	0.01138	0.01139
20°		0.01008	0.01003	0.01008	0.01005	0.01006	0.01006	0.01003

and water, alcohol was drawn in and then completely removed by many washings with the purest water. Hereby no air at all was sucked through the capillary tube. The water could now be undercooled to -9.30° . One viscosimeter was shattered by crystallization of the liquid contained in it, but a second instrument was made, by use of which the results in this article were in general obtained, which withstood repeatedly the solidification.

Table I gives results obtained with water from 20° to -9.30° , the viscosities being expressed in C. G. S. units. U and D in the first column signify whether the readings were taken as the liquid was passing up or down in the calibrated limb. The viscosity from 20° to 0° was determined by use of the larger volume AD, and from 0° to -9.30° , by the smaller volume AB.

In Table II a comparison of the results of various observers with ours is made.¹

CLARK COLLEGE
WORCESTER, MASS.

ON THE PINACOL-PINACOLIN REARRANGEMENT THE PREPARATION OF BENZOYLFORMIC ACID² AND SOME OF ITS DERIVATIVES

[FOURTH³ COMMUNICATION ON THE PINACOL-PINACOLIN REARRANGEMENT]

By S. F. ACREE

(This work was made possible by a grant from the Carnegie Institution of Washington.)

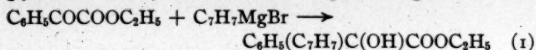
In the preparation of various symmetrical and unsymmetrical pinacols the choice of cheap starting materials is limited. It seemed desirable, therefore, to attempt the easy preparation of benzoylformic ester and its homologues in order to convert

¹ The results of most of the observers were taken from tables in Landolt-Börnstein's *Physikalisch-Chemische Tabellen*; those of Bingham and White from *Z. physik. Chem.*, **80**, 685 (1912).

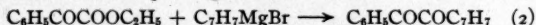
² This work was done in 1904-05. Other investigations took our attention away from the pinacol-pinacolin rearrangement, which we are now studying again.

³ *THIS JOURNAL*, **29**, 588; **33**, 180. *Ber. d. chem. Ges.*, **37**, 2753.

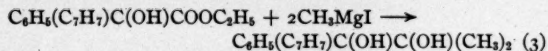
these first into the symmetrical and unsymmetrical dialkylglycollic esters by the use of the Grignard reagent:



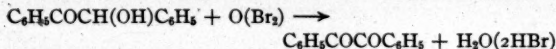
or into the corresponding orthodiketones:



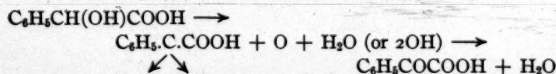
It was found that Reaction (1) takes place very easily. We had already¹ shown that the mono- and dialkylglycollic esters react very readily with the Grignard reagent and give pinacols in excellent yield, and we should now, therefore, be able to prepare unsymmetrical pinacols very easily:



A few years before this work was begun we had shown that weak oxidizing agents, such as bromine in chloroform, and potassium permanganate oxidize the secondary alcohols of this series of derivatives fairly readily into the corresponding diketones:



and the thought suggested itself that mandelic acid should be oxidized to benzoylformic acid in the same way:



The brilliant work of Nef,² Evans³ and others on this subject of oxidation and reduction encouraged us all the more, and it seems that Nef's theory of bivalent carbon offers the best explanation of such ready oxidations, as is seen in the above equations.

The benzoylformic acid is formed very readily, in excellent yields, by the interaction of mandelic acid and potassium permanganate in cold dilute solutions. The ester and the benzoylformyl chloride are readily formed from the acid. We

¹ Ber. d. chem. Ges., **37**, 2761, 2763.

² See the literature on this subject in Ann. Chem. (Liebig) and THIS JOURNAL.

³ J. Am. Chem. Soc., **38**, 1770, and earlier papers.

have undertaken further work along these lines, especially with lactic acid.

EXPERIMENTAL

The Preparation of Benzoylformic Acid, $C_6H_5COCOOH$, from Mandelic Acid.—Several different methods were tried, some of the details of which are given. The best results are obtained by rapid work. In one experiment, 100 grams of mandelic acid, neutralized with sodium hydroxide in one liter of water, was cooled with ice and treated slowly, during the course of 2 to 3 hours, with about 70 grams of potassium permanganate in as little water as possible. Alcohol was added to reduce the permanganate; the manganese dioxide was then filtered off and the solution acidified. About 20 grams of benzoic acid precipitated out and was removed by filtration. The filtrate was made neutral with alkali and evaporated to a small volume under 70 mm. pressure, acidified with sulphuric acid and extracted several times with ether, which was dried and distilled from the benzoylformic acid. The semisolid mass was mixed with carbon disulphide to dissolve the benzoic acid, well cooled and filtered. About 75 grams of the snow-white acid was thus obtained. When crystallized once more from carbon disulphide it melted at 63° – 64° , and 0.1547 gram required 10.50 cc. 0.1 N potassium hydroxide instead of the theoretical volume, 10.31 cc.

In another similar experiment, in which the oxidation required four days, only 40 grams of benzoylformic acid was obtained. The oxidation must evidently be done rapidly, to prevent the oxidation of the benzoylformic acid to benzoic acid.

In another experiment, 30 grams of mandelic acid was neutralized with sodium hydroxide and oxidized with 20 grams of potassium permanganate. After having been treated with alcohol and filtered, the solution was made neutral and, from necessity, allowed to stand overnight. The next day it was acidified and extracted several times with ether, which was dried and distilled. The residue of benzoylformic acid was treated twice with carbon disulphide to remove the benzoic acid, dissolved in ether and dried with calcium chloride. When

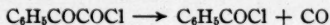
the ether was distilled off, there remained 27 grams of the liquid acid. This was then dissolved in 145 grams of absolute alcohol containing 7 grams of hydrogen chloride and heated 3 hours under a return condenser. When the alcoholic solution of the ester was poured into water, extracted with ether, dried and distilled *in vacuo*, only 15 grams of ethyl benzoylformate was obtained.

In another experiment, 50 grams of mandelic acid was oxidized with 35 grams of potassium permanganate, and the solution treated with alcohol and allowed to stand overnight. After the manganese dioxide was filtered off and the solution acidified, the benzoylformic acid was removed by repeated extraction with ether. The ethereal extract was dried and evaporated and an excess of alcoholic potash was added to precipitate the acid in the form of its potassium salt, of which 80 grams were obtained. The aqueous solution of this salt was acidified and extracted with ether. When the ether had been evaporated the liquid acid was dissolved in 330 grams of absolute alcohol containing 100 grams of hydrogen chloride and the mixture was boiled several hours. When the ester was isolated as usual, 45 grams were obtained and this was purified as follows: We converted 100 grams of sodium carbonate into sodium bisulphite in 200 cc. of water, and this was thoroughly shaken with the ester. The precipitate of the sodium bisulphite compound was filtered and washed with alcohol to remove any ethyl benzoate. The filtrate also gave another precipitate when the wash alcohol was added, and this second precipitate was washed with alcohol. The two precipitates were suspended in 300 cc. of water and decomposed with hydrochloric acid at an elevated temperature, the ester precipitating out. When this was extracted with ether, dried and distilled, 35 grams of pure ester, boiling at 265° under 766 mm., was obtained, together with about 9 grams of crude ester. The ester boils at 125° under 9 mm., gives the characteristic color test with concentrated sulphuric acid and thiophene in benzene and yields the sodium bisulphite compound when shaken with a 40 per cent. solution of sodium bisulphite. Some of the ester was made from the pure acid and analyzed.

0.1298 gram substance gave 0.3191 gram CO_2 and 0.0690 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_{10}\text{O}_2$	Found
C	67.38	67.05
H	5.67	5.91

Benzoylformyl Chloride, $\text{C}_6\text{H}_5\text{COCOC}\text{Cl}$.—When 10 grams of benzoylformic acid was boiled with a slight excess of thionyl chloride, SOCl_2 , at 100° , we obtained only benzoyl chloride. The benzoylformyl chloride had apparently decomposed at some stage in the operations, with the loss of carbon monoxide:



But by warming the same amounts at about 40° and fractionating the mixture under 9 mm., we got a small quantity of benzoyl chloride in the first fraction and then 6 grams of benzoylformyl chloride, which boiled at 125° under 9 mm. This acid chloride has an odor resembling that of benzoyl chloride. When treated with absolute alcohol, warmed and distilled, the acid chloride yielded the pure ester, which boiled at 125° under 9 mm. This ester gave the characteristic color tests and sodium bisulphite compound mentioned above. The ester was analyzed.

Analysis:

0.1571 gram of the substance gave 0.3858 gram CO_2 and 0.0861 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_{10}\text{O}_2$	Found
C	67.38	66.98
H	5.67	6.08

On the Action of Three Molecules of Phenylmagnesium Bromide on Ethyl Benzoylformate: Benzpinacol.—Fifteen grams of bromobenzene and 3 grams of magnesium were boiled 1 hour in 50 cc. of absolute ether, and 5 grams of the ester in 25 cc. of dry ether was added slowly. As each drop of the solution of the ester touched the solution of the Grignard reagent a white precipitate formed which dissolved when the solution

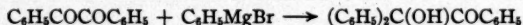
was shaken. The mixture was boiled 2 hours, cooled and added to cold, dilute sulphuric acid. The ethereal layer was dried with calcium chloride and distilled. When the benzpinacol began to precipitate, 50 cc. of absolute alcohol was added and the remainder of the ether was removed by distillation. The alcoholic solution was cooled to -10° and filtered from benzpinacol, which weighed 8.2 grams and melted at 186° – 187° . The filtrate gave more of the crude benzpinacol.

Analysis:

0.1420 gram substance gave 0.4438 gram CO_2 and 0.0819 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_{10}\text{O}_2$	Found
C	85.20	85.24
H	6.07	6.41

On the Action of Equimolecular Quantities of Phenylmagnesium Bromide and Ethyl Benzoylformate: Ethyl Benzilate.—In another article¹ it was shown that when an ethereal solution of the Grignard reagent is added to an ethereal solution of benzil, only one of the two carbonyl groups is attached and phenylbenzoin is formed:



Work with the benzoylformic ester offers the same possibilities and it is purely a question of experiment to learn whether the carbonyl adjacent to the phenyl group or that in the ester group (or both) adds the Grignard reagent and forms ethyl benzilate or benzil. The reactions are found in the theoretical part in Equations (1) and (2).

The experiments show that ethyl benzilate is formed in excellent yield. Ten grams of bromobenzene and 2 grams of magnesium in 50 cc. of ether were heated 1 hour and then slowly siphoned into 10 grams of ethyl benzoylformate in 100 cc. of cold ether. With each drop was formed a precipitate of the bromomagnesium salt of the ethyl benzilate. When all of the Grignard reagent had been added, the white pre-

¹ Ber. d. chem. Ges., 37, 2753.

precipitate was filtered, washed once with absolute ether and shaken thoroughly with water. The ethyl benzilate and magnesium hydroxide precipitated and the latter was dissolved by the addition of dilute sulphuric acid. The ester was dissolved in ether, dried with calcium chloride and obtained as an oil weighing 9.0+ grams when the ether was evaporated. This liquid gave, with concentrated sulphuric acid, the beautiful color characteristic of ethyl benzilate and benzilic acid, but also the violet color characteristic of ethyl benzoylformate when benzene containing thiophene was added. When the mixture was fractionated *in vacuo* to separate the esters, we obtained 6 grams of ethyl benzilate, boiling at 194°-195° under 10 mm., and 3 grams of a mixture boiling at 130°-193° under 10 mm. The pure ethyl benzilate gave a deep red color with concentrated sulphuric acid. When boiled a short time with alcoholic potash the ester was converted into potassium benzilate; when this salt was dissolved in water and treated with dilute sulphuric acid, a white precipitate of benzilic acid was obtained. This melted at 150°-151° alone or when mixed with another sample of the pure acid. The ester was analyzed.

Analysis:

0.2007 gram substance gave 0.5524 gram CO₂ and 0.1144 gram H₂O.

	Calculated for C ₁₁ H ₁₂ O ₃	Found
C	74.94	75.06
H	6.31	6.33

A similar experiment was tried with ethyl benzoylformate and *p*-tolylmagnesium bromide to obtain ethyl phenyl-*p*-tolylglycollate, C₆H₅(C₇H₇)C(OH)COOC₂H₅. Nearly all of the ethyl benzoylformate was recovered unchanged, but two grams of an ester boiling at 210°-212° under 15 mm. was also isolated. This has not yet been studied carefully.

A STUDY OF THE HYDROGEN ELECTRODE, OF THE CALOMEL ELECTRODE AND OF CONTACT POTENTIAL

[FOURTH¹ COMMUNICATION ON STUDIES OF ELECTROMOTIVE
FORCE]

By C. N. MYERS AND S. F. ACREE

(We are indebted to the Carnegie Institution of Washington
for aid in this work.)

I. INTRODUCTION

In a previous article,² the object of this investigation was stated as being the need of a direct, *very rapid* and accurate method for determining the hydrogen (also hydroxyl) ion concentration of dilute solutions. Such a method would be of special value in the study of many *organic* reactions involving, for example, the hydrolysis of salts or the saponification of esters; the reactions of addition products in cases of catalysis by hydrogen ions, and many others in which the system is gradually changing. The methods commonly in use heretofore have presented serious difficulties in their general application.

The work of H. G. Denham,³ who measured the degree of hydrolysis of several inorganic salts and of aniline hydrochloride, has been particularly suggestive for the reason that he obtained results agreeing extremely well with those determined by Bredig by the conductivity method. The hydrogen electrode has been recognized by several⁴ as a possible instrument for the solution of this problem, and with this in view the continuation of the present investigation has led to an attempt to make the hydrogen electrode an accurate instrument for measuring hydrogen ion concentrations; in other words, to make it a standard electrode.

In continuing this investigation, it was realized early that

¹ THIS JOURNAL, 46, 585, 621, 638.

² *Ibid.*, 46, 585 (1911).

³ J. Chem. Soc., 93, 41 (1908).

⁴ Desha: Diss., Johns Hopkins Univ., 1909. THIS JOURNAL, 46, 638. Loomis and Acree: *Ibid.*, 46, 585-621. Lapworth, in private communications, and articles in the J. Chem. Soc.

much of the accuracy of the work would be dependent upon the constancy and ease of reproduction of the calomel electrodes which were used with the hydrogen electrode. Furthermore, it seemed wise to make a more careful study of the hydrogen electrode than had been done by any one previous to this time. Upon investigation, it was found that considerable care in keeping the electrodes over long periods was quite essential in making the manipulation satisfactory, as well as accurate. More will be said concerning this particular point under the proper topic. To make the hydrogen electrode an accurate instrument for measuring hydrogen ion concentrations and to make the calomel cell more nearly standard, the measurements had to be made with a much higher degree of accuracy than has ordinarily been done up to the present time. In order to attain this result, the method of approaching the problem under consideration resolved itself into five lines of investigation:

I. A thorough and careful study of the calomel electrode. About sixty separate electrodes, arranged in batteries of ten, were prepared and intercompared with each other, so that the value adopted for the potential of the calomel electrode was the average of a number and not dependent upon a single electrode. Great care regarding purity of chemicals and cleanliness of apparatus was especially emphasized. Constancy and reproducibility under varying conditions were finally studied, the time period in some cases being as great as thirty (30) months.

II. Care of hydrogen electrodes and methods of keeping them constant so that they may be ready for use at any moment. Particular care was also taken in standardizing the acid used.

III. Measurements of the different systems. In order to obtain the most satisfactory measurements, it was found that there was need of considerable skill in manipulation, as well as of having both systems in the best possible condition previous to the comparison.

IV. Improvements in the apparatus. Temperature regulation has been found to be a very important factor in the measurement of the systems, so extreme precautions were

taken along this line in the way of contacts on the relays, use of the master relay, cooling coil, heating coil of nichrome wire wound so that the amount of current could be easily regulated by means of switches. New¹ batteries for calomel electrodes, constant pressure apparatus and devices for keeping conditions constant were installed with most gratifying results.

V. Measurements of the following systems:

- (a) H_2 -Pt-0.1 N HCl
- (b) 0.1 N KCl-HgCl-Hg
- (c) 0.1 N HCl-HgCl-Hg
- (d) Hg-HgCl-0.1 N HCl-0.1 N KCl-HgCl-Hg
- (e) H_2 -Pt-0.1 N HCl-0.1 N HCl-HgCl-Hg
- (f) H_2 -Pt-0.1 N HCl-0.1 N KCl-HgCl-Hg
- (g) Hg-HgCl-0.1 N HCl ^{Sandfällung} 0.1 N KCl-HgCl-Hg
- (h) Hg-HgCl-0.1 N HCl ^{sat. KCl} 0.1 N KCl-HgCl-Hg

A few of the difficulties encountered in the use, the preservation and the reproducibility of the hydrogen electrode will be briefly described in this preliminary paper. First of all, we have not found in the literature any suggestion as to how to preserve the hydrogen electrode over long periods of time under conditions that would insure a degree of activity and constancy in keeping with the efforts of this investigation. It has been found very essential to keep the electrode in an *active* condition all of the time if the electrode is to be reproduced to within 0.00001 volt. This limit of reproducibility can be obtained quite easily with the proper care, and even better agreement is attainable, as some of our tables will show. During the previous summer the *dry* electrodes were carefully placed in a closed box with raw cotton. In the fall they were placed in 0.1 N hydrochloric acid and saturated with hydrogen, but the agreement between the individual electrodes was very poor, as will be noted in the first three lines of Table IV. After becoming dry and remaining so for some time, it is impossible to saturate the electrodes completely with hydrogen, as the platinum black is not in a condition to take up the hydrogen or even hold it. It became apparent at once

¹ These do not have the ground-glass caps used by Loomis (THIS JOURNAL, 46, 595, 597, etc.), but are constricted and sealed at the top.

that the most satisfactory method of *overcoming* this trouble was to *obviate* the difficulty in the first place. The electrodes were again electroplated with platinum black as described in the previous article, and considerable plating was required before they gave satisfactory agreement. However, all the electrodes (17 in number) were replatinized and, after some trouble, were made to agree to within about 0.00001 volt.

Among the other difficulties encountered were the effects of small amounts of impurities which were being dissolved from the commercial rubber stoppers¹ by the hydrochloric acid in which the electrodes were placed. A rubber stopper with 18 holes held the electrodes in place; in order to test their constancy, the electrodes must necessarily be in the acid for long intervals. We wanted them in measuring condition all the time. In order to avoid these impurities, a special mould was ordered in which *pure gum* stoppers were made for us and no further trouble was experienced. These are only a few incidents which show the sensitiveness of the hydrogen electrodes for detecting small amounts of foreign substances.

If satisfactory methods for measuring or calculating contact potential between various solutions were at hand, the hydrogen electrode could not be surpassed as an instrument for obtaining the ionization values of acids. If the hydrogen electrode is to be a standard electrode, it must be subjected to mechanical disturbance, transportation and use. In all of these particulars, experiment has shown the hydrogen electrode to be very satisfactory. The glass tube of one electrode became cracked at the place where the platinum wire is sealed into the electrode tube, and it was carefully wrapped and the glass sealed together with *no measurable bad effect* whatever on the electrode. Then again, the electrodes are moved around, taken out of the cylinders while acid is being replaced, and yet the same values for the individual electrodes are obtained as soon as saturation with hydrogen is reached. In comparing various systems involving the use of the hydrogen

¹ For a description of the apparatus, see Loomis and Acree: *THIS JOURNAL*, 44, 602.

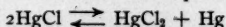
electrodes, these may be in use for four hours at a time and no change greater than the experimental error is ever detected.

Another device for obtaining better agreement between the individual electrodes, and *doing so in a very short time*, consists in the use of a short-circuiting arrangement in which all of the hydrogen (or calomel) electrodes are connected with each other through the mercury in the electrode tubes. We have termed this device a "crowfoot," and it is in use at all times when experiments are not being carried on. It will be seen at a glance that a much better agreement between the individual electrodes is obtained in a short time by its use. Occasionally, the electrodes will not show a variation greater than 0.000003 volt. This same device is used in connection with the calomel electrode with equally good results. When all of the different electrodes of a new calomel battery are connected by the "crowfoot," they attain values agreeing to within 0.00001 volt in about 2 days. If the "crowfoot" were not used, it would take about 5 days for them to agree as closely. As many as 40 hydrogen electrodes have been in use at one time. It seems better to use a great many electrodes, so that a measurement is not dependent upon one electrode but is the result of a comparison of a large number of them. No measurement is ever made unless all of the electrodes show a satisfactory agreement among themselves. The constancy of the electrodes has been tested over a period of nearly two years. It has been found that the amount of platinum black deposited on the electrodes is a factor which influences the relation between the individual electrodes. It is well known that changes in barometric pressure influence the concentration of hydrogen in the electrode and the solutions, so there is a lagging effect sometimes. It is quite analogous to the lagging effect noted in osmotic pressure. The point is that an electrode with a great deal of black on it does not respond as quickly to changes in the barometer and, hence, to changes in the amount of hydrogen present, thus causing changes in the individual readings of the potential of the electrodes. In due time, however, the values become more uniform; *i. e.*, saturation or changes in the degree of saturation are responded to finally. Of course,

these changes of potential are not large, but when it is considered that 0.001 of an atmosphere causes a change of 0.000025 volt, it is easily seen that a few millionths of a volt can be the result of a sudden change in the barometer. Table IV gives a few points in the history of the electrodes.

Several investigators, and especially Bjerrum, have observed that in measuring any system in which the hydrogen electrode is a part there is a change in the value obtained at the beginning and an hour later, perhaps. This statement has led Dr. Myers to study this point to some extent, but we believe that we can offer a satisfactory explanation. If the systems 0.1 N KCl-HgCl-Hg and 0.1 N HCl-Pt-H₂ are to be compared, it is possible to connect them by satisfactory means and still obtain a changing value for the system if it is not first saturated with hydrogen. But suppose that the connecting system is first saturated with hydrogen, or, in other words, equilibrium is established and the systems are connected. Observations over periods of even a couple of hours show no changes whatever, provided no barometric change has taken place. Considerable emphasis has been given to this phase by Dr. Myers and we believe that in comparing these systems we are reasonably sure of our results to within 0.05 millivolt. Finally, it is our opinion that with saturated systems no changes in the value for any given system take place, other conditions remaining constant.

It is a well-known fact that the standard Clark or Weston element shows a gradual shift in its value, depending a great deal upon the age of the element. A similar shift has been observed by us in connection with the calomel electrode. In order to study this case, batteries have been made up from time to time and intercompared. At the present time, and with our present data, it appears that after standing a year the changes are very slow. We believe, as many others do, that this change or shift downward is due to the decomposition of the calomel:



At present, we have a pair of cells containing mercuric chloride in the presence of ordinary calomel and will compare these with old batteries. It would be expected that the relation of

the potentials of the two systems would be practically zero if equilibrium is brought about quickly by mercuric chloride.

Only a few of the tables showing the relation of the various systems to each other are given in this paper. It should be stated here that we find the "Sandfüllung" method of Bjerrum very satisfactory and have used it to much advantage. A description of apparatus and technique will follow in later articles, in which measurements at constant temperature and constant pressure will be given. Constant pressure apparatus and a Fuess barometer accurate to within 0.05 mm. are used in connection with these systems.

Our reference cells are several Weston cells loaned us by the National Bureau of Standards and compared with their standards from time to time by Mr. E. C. McKelvey and Mr. Schumacher. We are greatly indebted to these gentlemen for much valuable advice and kindly interest. At present we are using 5 cells, Nos. 115, 117, 158, 197 and 201, and at other times we have used also Nos. 228, 231 and 251. That these standards check each other very closely is shown by the measurements given us on Oct. 4, 1912, for 28°:

Cell	115	117	158	197	201
E. m. f.	1.017847	1.017860	1.017838	1.017847	1.017851

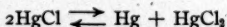
These values are based on the international volt, which is taken as 1.0000/1.0183 of the electromotive force of the Weston normal cell at 20°. The temperature of our bath is 25° and the electromotive force at 25° is, therefore, 0.000155 volt greater than the above values. The average value of the five cells at 25° is, therefore, about 1.018000 volts. We check the cells against each other at frequent intervals on our potentiometer to assure ourselves that they are all in excellent agreement.

Our potentiometer was made for use with standard cells with the definition of the volt used prior to Jan. 1, 1911, and the lowest figure on the standard cell dial is 1.01850. Our cells set on this figure have really the value 1.01802, so all readings on the potentiometer must be corrected for the calibration of the potentiometer and then multiplied by 1.01802/1.01850. In addition we must add 0.000015 volt to those readings involving the hydrogen electrode, because of an error

which we found in our old barometer when it was compared with a fine Fuess Normal Barometer. In the tables we give first the readings observed on the potentiometer and then the final reading, which we describe as "cor. ave." or "cor. value."

Experimental

In Table I we give the incomplete record of a 0.1 N KCl-HgCl-Hg battery, showing the changes taking place from the time the battery was first prepared. The numbers at the top of each column designate the number of each cell which composes the battery. All of the batteries are composed of ten cells each and this gives us an average value for this system for the reason that we always compare the entire set before making a measurement. These values are chosen haphazard and are a fair sample of the record of this battery. Six of these batteries have been prepared and intercompared so that the table also represents a fair record of the other batteries. It will be seen that about 36 to 48 hours are necessary for the cells to settle down, and over a period of twelve months the relation of the cells to No. 1, chosen as a standard, has remained approximately constant. It is not to be understood that the entire system has not changed, for it has done so (see Table IIc), in conformity with the observations of many others, probably as the result of a disintegration of the calomel in the following manner:



The total change amounts to 0.000085 volt in a period of eight to ten months. Using the data of Abegg, in which the Hg^+ ion concentration is given as 235 times as great as the Hg' ion concentration, we get a value 0.000090 volt, which is in close agreement with the experimental value found. Experiments in which mercuric chloride in extremely small amount is present are being carried out. The change observed between the individual cells of the calomel battery is smaller than in the case of the standard Weston element. The following values have been assigned to one of the elements by the U. S. Bureau of Standards: 1.01892, 1.01887, 1.01883 and 1.01783. Our total change in a battery has amounted to 0.000085 volt in one year, but the individual cells never vary this much.

Table I—Battery No. IV, 0.1 N KCl-HgCl-Hg¹

Prepared May 2, 1912

18 hours after preparation the following values were recorded

Date	With Wires									
	2	3	4	5	6	7	8	9	10	
May 3, 1912	0.000140	0.000041	0.00001	0.000038	0.000026	0.00005	0.000025	0.000055	0.00018	
May 4, 1912	0.000011	0.000005	0.000012	0.000008	0.000008	0.00008	0.000035	0.000002	0.000004	
May 6, 1912	0.000015	0.000004	0.000006	0.000011	0.000004	0.000007	0.000002	0.000009	0.000005	
May 7, 1912	0.000012	0.000007	0.000010	0.000013	0.000002	0.00003	0.000012	0.000015	0.000011	
May 9, 1912	0.000001	0.000009	0.000009	0.000011	0.000010	0.000016	0.000010	0.00001	0.00003	
Without Wires										
May 11, 1912	0.00005	0.00006	0.000015	0.00007	0.00006	0.00009	0.000045	0.00008	0.000075	
With Wires										
May 22, 1912	0.000008	0.000009	0.000003	0.000007	0.000007	0.000010	0.000001	0.000009	0.000010	
Apr. 11, 1913	0.000008	0.000007	0.000006	0.000007	0.000007	0.000007	0.000008	0.000008	0.000005	

¹ In this article we have omitted the signs showing whether these cells are + or — when compared with the reference cell. All such data will be presented in the final reports.

Table IIa shows an intercomparison of two freshly prepared calomel batteries by using Cell No. I of each battery as the standard electrode. Table IIb compares the same two batteries after a period of one year. The agreement in this latter case is even better than at the first comparison. The short-circuiting system is always used. In Table IIc the relation between a freshly prepared calomel battery and one of a year's standing is given. The new battery is negative with respect to the old one, as would be expected. In the first three months, the difference of potential between the same batteries was about 0.000045 volt.

Table II—Comparison of Batteries B_{IV} and B_V
0.1 N KCl-HgCl-Hg

Cell	^a By compared against Cell I of B_{IV}		^b By compared with B_{IV} after 1 year. Cell I of B_V used as standard electrode	^c By compared with a fresh calomel battery
	May 9	May 14		
1	0.000004	0.000007	0.000000	+0.000084
2	0.000001	0.000004	0.000003	0.000087
3	0.000007	0.000010	0.000000	0.000096
4	0.000009	0.000006	0.000002	0.000088
5	0.000010	0.000002	0.000002	0.000085
6	0.000009	0.000006	0.000002	0.000087
7	0.000010	0.000007	0.000006	0.000082
8	0.000004	0.000001	0.000004	0.000080
9	0.000009	0.000006	0.000006	0.000087
10	0.000003	0.000001	0.000001	0.000087

Table III gives a record of another battery, in which its history is very marked. Some oil got into the battery shortly after it was first made, but we decided to study the history of such a poor system and now give the data. The effect of the use and the non-use of the short-circuiting system is very clearly shown in this table. Where the words "without wires" appear, it indicates that the short-circuiting system was removed on the date appearing above these words. We realize that it is not one of our best batteries, but it shows that with a little trouble the reproducibility of the system is surely as good as 0.00001 volt. As stated above, a little oil crept in accidentally and for that reason the battery was not considered satisfactory and was prepared anew.

Table III—Battery No. II, 0.1 N KCl-HgCl-Hg

Prepared March 8, 1912. Electrode 1 as Standard

Readings taken two hours after the battery was placed in the bath

Date	2	3	4	5	6	7	8	9	10
Mar. 8	0.000460	0.000325	0.000300	0.000152	0.000370	0.000307	0.000570	0.000475	0.000120
Mar. 11	0.000134	0.000140	0.000103	0.000022	0.000082	0.000120	0.000185	0.000100	0.000035
Mar. 12	0.000065	0.000095	0.000045	0.000000	0.000046	0.000087	0.000125	0.000057	0.000024
Mar. 13	0.000095	0.000112	0.000070	0.000024	0.000018	0.000030	0.000072	0.000020	0.000000
Mar. 14	0.000085	0.000104	0.000060	0.000000	0.000062	0.000082	0.000100	0.000047	0.000055
	Without Wires								
Mar. 15	0.000127	0.000160	0.000100	0.000045	0.000105	0.000122	0.000157	0.000065	0.000000
	With Wires								
Mar. 16	0.000085	0.000110	0.000075	0.000075	0.000045	0.000100	0.000120	0.000070	0.000015
Mar. 19	0.000050	0.000073	0.000021	0.000000	0.000016	0.000030	0.000052	0.000013	0.000010
	Without Wires								
Mar. 20	0.000082	0.000113	0.000020	0.000010	0.000024	0.000045	0.000082	0.000013	0.000020
	With Wires								
Mar. 22	0.000030	0.000060	0.000002	0.000017	0.000001	0.000010	0.000035	0.000007	0.000030
Mar. 27	0.000035	0.000035	0.000000	0.000008	0.000004	0.000000	0.000005	0.000000	0.000026
Apr. 1	0.000022	0.000022	0.000007	0.000000	0.000002	0.000004	0.000005	0.000002	0.000004
Apr. 3	0.000020	0.000023	0.000006	0.000000	0.000000	0.000012	0.000008	0.000009	0.000002
	Without Wires								
Apr. 5	0.000055	0.000062	0.000037	0.000050	0.000012	0.000035	0.000025	0.000037	0.000030
	With Wires								
Apr. 9	0.000026	0.000026	0.000007	0.000001	0.000005	0.000016	0.000005	0.000012	0.000020
Apr. 12	0.000022	0.000020	0.000020	0.000022	0.000009	0.000024	0.0000120	0.000015	0.000007
Apr. 18	0.000015	0.000018	0.000004	0.000005	0.000007	0.000006	0.000004	0.000008	0.000022
Apr. 24	0.000006	0.000006	0.000005	0.000001	0.000005	0.000004	0.000003	0.000004	0.000002

Oil crept in before sealing and battery taken down

Table IV— H_2 -Pt-0.1 N HCl. Stopper I

Electrodes were placed in 0.1 N HCl after being left in box three months. H_2 allowed to run about five hours before first record was taken. Electrode 10 chosen as standard

Date, 1912	9	8	7	6	5	4	3	2	1
Jan. 18	0.000186	0.00082	0.00047	0.00070	0.06203	0.000586	0.058810	0.000155	0.02558
Jan. 19	0.000232	0.000178	0.000168	0.000169	0.004988	0.001736	0.003445	0.000696	0.00082
Jan. 20	0.000175	0.000081	0.000101	0.000195	0.002654	0.000895	0.001720	0.000405	0.000435
Electrodes replatinized and treated as described									
Jan. 22	0.00005	0.000075	0.000227	0.00003	0.00636	0.000218	0.00043	0.000097	0.000073
Began use of "Crowfoot." Replatinized and electrolyzed									
Jan. 24	0.000015	0.000035	0.0000525	0.00004	0.000098	0.000031	0.000015	0.000015	0.000047
Jan. 26	0.000006	0.000010	0.000010	0.000010	0.000046	0.000009	0.000005	0.000025	0.000013
Jan. 27	0.000007	0.000003	0.000000	0.000005	0.000010	0.000006	0.000000	0.000004	0.000002
Jan. 31	0.000010	0.000006	0.000006	0.000003	0.000028	0.000006	0.000006	0.000037	0.000004
Rubber dissolving in acid as shown below									
Feb. 1	0.000042	0.000025	0.000046	0.000014	0.000046	0.000028	0.000044	0.000078	0.000044
Apparatus cleaned. Electrodes and stopper boiled in distilled water									
Feb. 4	0.000011	0.000015	0.000012	0.000006	0.000010	0.000018	0.000012	0.000025	0.000025
Feb. 6	0.000004	0.000001	0.0000025	0.000003	0.000003	0.000008	0.000002	0.000002	0.000005
Stove in bath burned out and temperature drops 6 degrees									
Feb. 9	0.000006	0.000003	0.000003	0.000005	0.000004	0.000002	0.000006	0.000006	0.000001
Without Wires									
Feb. 17	0.000025	0.00001	0.000015	0.000015	0.000014	0.000012	0.000009	0.000015	—
Feb. 19	0.000020	0.000003	0.000015	0.000015	0.000026	0.000026	0.000025	0.000034	0.000027
Rubber dissolving in acid									
Mar. 6	0.00005	0.00006	0.00013	0.000055	0.000115	0.00009	0.00005	0.00014	0.000056
Electrodes boiled in distilled water and electrodes placed in constant pressure desiccator									
June 1	0.000020	0.000003	0.000005	0.000002	0.000003	0.000001	0.000001	0.000003	0.000000
Apr. 25,									
1913	0.000005	0.000003	0.000006	0.000006	0.000007	0.000005	0.000004	0.000001	0.000003

¹ This electrode was broken and taken to Washington for repairs. When brought back to Baltimore on the same day and saturated again with hydrogen the values given below were obtained.

In Table IV, a record of the hydrogen electrode is given. In all, there are about 40 in use and only one section is given here. The record in this table shows the disagreement of the electrodes after standing dry all summer and the difficulty of getting them into close agreement. Many more readings have been recorded but these illustrate the essential changes. It should be noted that there is little change in the relation of the electrodes to each other on June 1 and on April 25, a period of nine months or more. The hydrogen electrode is reproducible to within 0.00001 volt, although the table shows even better agreement. This table also shows that the electrode is available at almost any moment when it is desired for use. The remaining electrodes are equally as good.

In Table Va a typical comparison of the hydrogen and *fresh calomel electrodes* and the methods of applying the correction are shown. The values *a, b, c, d* are each averages of ten values and have been corrected for the old barometer. Of the total 760 mm. pressure to which each of these readings corresponds, about 23.5 mm. is the partial pressure of the vapor above the acid and the remainder, about 736.5 mm., is the partial pressure of the hydrogen. In Table Vb an average of 120 readings is given. These values are obtained by using different decinormal batteries on different dates, which means that the H^+ ion concentration of the different hydrogen electrodes was perhaps slightly different at each time. The first six averages show increasing values, which would be expected for the reason that the calomel battery changes gradually and hence the potential of the system should increase. If, however, these values are all corrected for aging, it is found that the corrected average in Column 3 is 0.426910 volt, which is in very close agreement with all the values in Table Va, and with the last four values in Table Vb, which were obtained on Dec. 13, 1912, with two *fresh calomel batteries*.

Table Va— $\text{Hg-HgCl-0.1 N KCl-0.1 N HCl-Pt-H}_2$ Bar. in atms., 1.010; cor. in e. m. f., -0.000230

0.427341	
0.427342	
0.427336	Other similar averages
0.427342	0.427106 (a)
0.427335	0.427109 (b)
0.427342	0.427109 (c)
0.427340	0.427108 (d)
0.427335	
0.427338	Ave., 0.427108
0.427340	Cor. ave., 0.426918
Ave., 0.427339	
Bar. cor., 0.00023	
0.427109	
Cor. ave., 0.426919	

Table Vb

Apr. 1, 1912	0.427090	0.427090
Apr. 19, 1912	0.427108	0.427098
May 9, 1912	0.427112	0.427092
May 9, 1912	0.427115	0.427095
May 23, 1912	0.427123	0.427098
May 23, 1912	0.427126	0.427109
Dec. 13, 1912 ¹	0.427106	0.427106
	0.427109	0.427109
	0.427109	0.427109
	0.427108	0.427108
Ave., 0.427116		0.427100
Cor. ave., 0.426926		0.426910

Table VIa gives a typical experiment and VIb an average of all such average readings taken when Bjerrum's "Sandfüllung" was used between the calomel and hydrogen electrodes. The final average represents about 100 separate electrode readings. The system compared is given at the top. The use of the "Sandfüllung" was to prevent the diffusion of the liquid from one system to the other.

¹ These last four values were obtained from fresh calomel batteries.

Table VI— Hg-HgCl-0.1 N HCl ^{Sandfällung} 0.1 N HCl-Pt-H_2

a		b
Bar. in atms., 1.004		Corrected averages
Cor in c. m. f., -0.00010		
0.400100		
(0.400470)		
0.400080		0.400031
0.400070		0.400081
0.400080		0.400036
0.400090		0.400020
0.400090		0.400020
0.400090		0.400020
0.400070		
0.400045		
	Ave., 0.400035	
	Cor. ave., 0.399858	
Ave., 0.400080		
Bar. cor., 0.000100		
0.399980		
Cor. ave., 0.399803		

Tables VIIa, VIIb and VIIc give average values for the systems in question. When saturated potassium chloride was used in the connecting siphon, experiments with and without the "Sandfällung" were carried out and no difference in the value of the potential was found.

Table VIIc gives a typical contact potential experiment by the use of one Hg-HgCl-0.1 N HCl battery against a *fresh* calomel battery. It is plainly seen that the individual values are not as uniform as in the other systems but they are as good as the $0.1 \text{ N HCl-HgCl-Hg}$ system is by itself. An average of several such averages is given in the other part of the table, showing the value placed for contact potential. No changing values are observed in this comparison. Readings were taken over a period of a couple of hours and they remained constant.

Table VIIa— $\text{H}_2\text{-Pt-0.1 N HCl}$ ^{Sandfällung} 0.1 N KCl-HgCl-Hg

Ave. value for system
0.40120
0.40114
0.40120
Ave., 0.401180
Cor. ave., 0.401003

Table VIIb— H_2 -Pt-0.1 N HCl— $\frac{Sat. KCl}{0.1 N KCl}$ -HgCl-Hg

Ave. value for system

0.401200

0.401140

0.401200

0.401264

Ave., 0.401200

Cor. ave., 0.401023

Table VIIc—Hg-HgCl-0.1 N KCl-0.1 N HCl-HgCl-Hg
Contact PotentialSeveral sets of values
averaged

0.027863

0.027760

0.027775

0.027795

Ave., 0.027798

Cor. ave., 0.027785

Readings from one

Hg-HgCl-0.1 N HCl battery

0.028100

0.027910

0.027690

0.028190

0.027610

0.027610

0.027660

0.027562

0.027610

0.027806

Ave., 0.027775

Cor. ave., 0.027762

This entire work will be summed up in a later article which will appear as a monograph. All apparatus and methods of experimentation will then be described in detail. One conclusion to be drawn at this time is the constancy in values of the various systems mentioned, which is explained by obtaining complete saturation with hydrogen before joining them.

JOHNS HOPKINS UNIVERSITY

June 1, 1913

[Contributions from the Chemical Laboratory of Harvard College]

ON THE PERKIN REACTION: A REPLY TO THE
CRITICISM OF H. MEYER AND BEER¹

BY ARTHUR MICHAEL

W. H. Perkin² found by heating benzoic aldehyde with acetic anhydride and sodium acetate, butyrate or valerate

¹ Monats. Chem., **34**, 649 (1913).² J. Chem. Soc., **31**, 388 (1877).

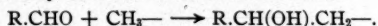
to 180° that in all cases cinnamic acid alone is formed and he concluded from these results that the reaction proceeds between the aldehyde and anhydride and not between the aldehyde and the salt. Fittig and Slocum¹ then took up the study of the mechanism of the Perkin synthesis and showed that heating a mixture of benzoic aldehyde, acetic anhydride and sodium acetate to 100° caused no reaction; when sodium butyrate in the place of the acetate was used, phenylangelic acid alone was slowly formed, but, when the experiment was done at 150°, a mixture containing 1 part of the above to 2 parts of cinnamic acid was obtained, and at 180° the proportion was 1 part of the first to 10 parts of the latter acid. Fittig² concluded from these results that at 100° the reaction proceeds between aldehyde and salt and explained the formation of cinnamic acid at higher temperature by assuming that the anhydride, under these conditions, first reacts on the salt to form sodium acetate. Therefore, according to this interpretation of the Perkin synthesis, which was generally accepted, it always proceeds between aldehyde and salt. Michael and Hartman³ were led by theoretical considerations to doubt the validity of Fittig's proofs. They showed experimentally that it is only necessary to heat acetic anhydride for a short time at 100° with the sodium salts of butyric and caproic acids to obtain butyric and caproic anhydrides in excellent yields, while butyric anhydride does not act noticeably on sodium acetate under these conditions. These results prove unmistakably that in the Fittig and Slocum experiment of heating the aldehyde, acetic anhydride and sodium butyrate at 100°, the contents of the tube, after a short heating, must have consisted of aldehyde, considerable butyric anhydride and sodium acetate and but little, if any, acetic anhydride and sodium butyrate. As the reactions in the Perkin synthesis proceed very slowly, the formation of only phenylangelic acid under these conditions is a conclusive proof that the reaction proceeds between aldehyde and butyric anhydride with sodium acetate acting as a catalyzer, and, further, that Fittig's

¹ Ann. Chem. (Liebig), **277**, 53 (1885).

² *Ibid.*, **277**, 48.

³ Ber. d. chem. Ges., **34**, 918 (1901).

explanation of the formation of cinnamic acid at higher temperatures cannot be correct since sodium acetate was present in large proportion in the experiment at 100°, when no cinnamic acid was formed. Recently a further contribution to this interesting problem was made by H. Meyer and Beer,¹ who confirm Nef² in the fact that cinnamic acid is not formed by heating benzoic aldehyde, acetic acid and sodium acetate to 200°, but find that *o*-chlorocinnamic acid is obtained when a mixture containing *o*-chlorobenzoic aldehyde, instead of benzoic aldehyde, is subjected to these conditions. These chemists conclude, from this result, that the Perkin reaction does not proceed between the aldehyde and anhydride. A stable chemical system may become unstable by so changing one of its components as to increase its free *chemical* energy, by decreasing the chemical resistance which has to be overcome, or, if the reaction is dependent on the presence of a catalyzer, by using one of greater efficiency.³ The first phase in the Perkin synthesis involves an aldolization:⁴



If the first step in the reaction cannot proceed in a given system it may be brought about by using an aldehyde whose carbonyl group has more free *chemical* energy, or by so changing the chemical character of the radical joined to the methyl group that the expense of energy necessary to separate one of its hydrogen atoms from the methyl carbon is diminished. Benzoic aldehyde does not react with acetic anhydride and sodium acetate at 200°, but by introducing a negative atom, or group, in the ortho position to the formyl group of the aldehyde we increase considerably the free *chemical* energy of its carbonyl group, which is now able to overcome the resistance due to the separation of hydrogen from the methyl carbon. Although a mixture of benzoic aldehyde, sodium acetate and glacial acetic acid may be heated to 200° without formation of cinnamic acid, Meyer and Beer⁵ noticed its formation when potassium, instead of sodium, acetate is

¹ Monats. Chem., **34**, 649 (1913).

² Ann. Chem. (Liebig), **298**, 202 (1897).

³ Michael: J. Am. Chem. Soc., **32**, 990 (1910).

⁴ Fittig: Ann. Chem. (Liebig), **227**, 48 (1885).

⁵ Monats. Chem., **34**, 655.

used. This result is in accordance with the fact that potassium salts show a far greater capacity to effect aldolization than the corresponding sodium derivatives.¹ These chemists have shown, too, that chlorocinnamic acid may be made, without employing acetic anhydride or acid, by heating *o*-chlorobenzoic aldehyde and potassium acetate, but to effect this result it is necessary to subject the mixture to a considerably higher temperature (240°). There is, of course, no reason why this autocatalytic synthesis should not be realized if, with the aid of a high temperature, the reactive carbonyl of chlorobenzoic aldehyde is able to overcome the hindrance to aldolization.

The experiments of Meyer and Beer bring new evidence that the Perkin synthesis proceeds more difficultly with acetic acid than with acetic anhydride, and that it goes with still greater difficulty with potassium acetate. Instead, therefore, of disproving the view that, in the reaction of an aldehyde, acid anhydride and sodium salt of an aliphatic acid, which was solely the subject in the discussion of the Perkin reaction by Hartman and myself,² the first phase of the change consists of an aldolization between aldehyde and anhydride, they simply add a new set of facts to confirm this interpretation, which, indeed, is the only one in accordance with our present experimental knowledge of the subject.

[Contribution from the Chemical Laboratory of the University of Cincinnati]

APPLICATIONS OF THE ELECTRONIC CONCEPTION OF VALENCE

PART I. REACTIONS AMONG CERTAIN CLASSES OF COMPOUNDS CONTAINING NITROGEN

PART II. THE BECKMANN REARRANGEMENT

BY LAUDER WILLIAM JONES

INTRODUCTION

Very convincing arguments have been presented in support

¹ Michael and Kopp: *THIS JOURNAL*, 5, 182 (1883).

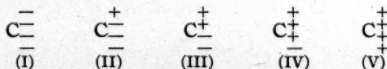
² The writer, therefore, does not consider the criticism of Meyer and Beer as relevant to the subject, nor is the fact (*Ibid.*, 34, 656) that with one salt—rubidium acetate—the yield of chlorocinnamic acid was somewhat larger with acetic acid than with acetic anhydride. Only when the conditions of the experiments are absolutely comparable and when they can be repeated with the same result, should they be used as the basis for theoretical deductions.

of the hypothesis which regards electricity to be of such a nature that it "reacts" with atomic weights of the chemical elements in unit quantities, and, therefore, in accordance with the laws of definite and of multiple proportions. Notwithstanding the completeness with which this view has been presented in the abstract, comparatively few chemists¹ have ventured upon applications of it to concrete problems in organic chemistry, by which alone its usefulness in this field may be put to the test. In terms of the conception of valence which this hypothesis proposes, the processes of oxidation and reduction may be regarded as an exchange of electrons between atoms, a loss of negative electrons corresponding to oxidation and a gain in negative electrons to reduction. Thus, if two atoms, A and B, are linked together, the compound may be represented by two electronic formulas:



If (I) passes to (II) by an exchange of negative electrons, A is said to be oxidized, while B is reduced.

Looked at from this angle, carbon with four as the valence of its atomic weight would show five stages in the series of oxidation and reduction, which may be illustrated by the following electronic symbols:²

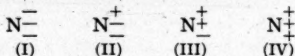


These symbols would represent the states of oxidation of the carbon atom in five compounds; viz., methane (I), methyl

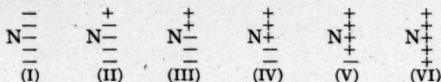
¹ Schuetzenberger: *Ann. Chem. (Liebig)*, **130**, 113 (1861). Seliwanow: *Ber. d. chem. Ges.*, **25**, 3612 (1892). Noyes and Lyon: *J. Am. Chem. Soc.*, **23**, 463 (1901). Stieglitz, *Ibid.*, **23**, 797 (1901); **29**, 51 (1903); *Science*, **30** (1907); *Qualitative Chem. Analysis*, I and II, p. 29 (1911); *Ibid.*, III, p. 82 (1911). Walden: *Z. physik. Chem.*, **43**, 407 (1903); **46**, 103 (1903). Abegg: *Z. anorg. Chem.*, **39**, 343 (1903). Thomson, J. J.: *Phil. Mag.*, March, 1904; "The Corpuscular Theory of Matter," p. 130 (1907). Nef: *J. Am. Chem. Soc.*, **30**, 645 (1908). Ramsay: *J. Chem. Soc.*, **93**, 774 (1908). Falk and Nelson: *School of Mines Quarterly*, **30**, 179 (1909); *J. Am. Chem. Soc.*, **32**, 1673 (1910); **33**, 1140 (1911); *Congress of Applied Science*, **6**, 282 (1912). Fry: *Z. physik. Chem.*, **76**, 385, 398, 591 (1911); **77**, 29 (1912); *J. Am. Chem. Soc.*, **34**, 664 (1912). Jones: *THIS JOURNAL*, **48**, 25 (1912). Noyes: *J. Am. Chem. Soc.*, **34**, 662 (1912); **35**, 767 (1913). Acree: *THIS JOURNAL*, **49**, 347 (1913).

² Fry: *Z. physik. Chem.*, **76**, 399 (1911). Stieglitz: *Science*, **30** (1907).

alcohol (II), formaldehyde (III),¹ formic acid (IV) and carbonic acid (V). Nitrogen presents a somewhat more complicated case. If it be considered as trivalent, and its two remaining or auxiliary valences disregarded, there are four types possible:

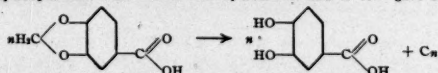


These symbols correspond to the states of oxidation of the nitrogen atom in ammonia (I), hydroxylamine (II), dihydroxylamine (hyponitrous acid) (III), and nitrous acid (IV). If quinquivalent nitrogen is represented in a similar way, there are six electronic symbols, exclusive of stereoisomeric configurations:



All but (I) yield compounds in corresponding states of oxidation with respect to the nitrogen atom. Thus, ammonium compounds correspond to (II); hydroxylammonium compounds and amine oxides, $\text{R}_3\text{N} : \text{O}$, to (III); isonitroparaffins to (IV); nitro compounds to (V); and derivatives of nitric acid to (VI). It will be noted that in all cases where nitrogen functions as trivalent, the two remaining or auxiliary valences must be one negative and one positive. Taking this into consideration the four symbols used to represent trivalent nitrogen become identical with symbols (II), (III), (IV) and (V), among those representing quinquivalent nitrogen.² Com-

¹ It is noteworthy that, taken as a whole, the carbon atom in formaldehyde is neither negative nor positive. This suggests an explanation of the observation that some of the derivatives of formaldehyde decompose and deposit elemental carbon. Thus, piperonylic acid when heated with hydrochloric acid to 150° gave carbon:

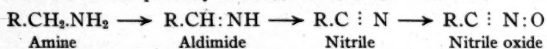


² Univalent nitrogen would be represented by the two symbols N^+ and N^- . The auxiliary valences must be two positive and two negative. That is, we should expect to obtain univalent nitrogen derivatives from compounds which contain nitrogen either in the state of oxidation corresponding to hydroxylamine, or to dihydroxylamine (hyponitrous acid), and from these alone.

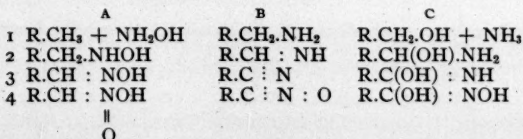
pounds represented by formulas containing nitrogen linked to nitrogen, N-N, may be indicated by proper combinations of the various symbols given.

Amines, Aldimides, Nitriles and Nitrile Oxides.—An inspection of the chemical transformations characteristic of four classes of organic compounds, viz., primary amines of the type $R.CH_3.NH_2$, aldimides, $R.CH:NH$, nitriles, $R.C:N$, and nitrile oxides, $R.C:N:O$ —and of a number of other organic compounds which may be grouped about them in a very intimate way—suggested certain applications of the electronic hypothesis which seem to throw new light upon the chemical relations between these compounds, and to indicate a mechanism in terms of which their transformations may be portrayed more precisely than by the ordinary structural formulas now in vogue.

If, for the sake of clearness only, the monomolecular forms are considered, these four compounds plainly represent a series of products which may be grouped as successive stages in the oxidation of the primary amine, $R.CH_3.NH_2$. Thus:



Each of the three oxidation products of the primary amine may be considered as a transition compound, and may be placed schematically between two isomers formally derivable from it by the addition of one molecule of water. The amine may also be included in this table, together with the products of hydrolysis which it may be imagined to yield by the breaking of the carbon-nitrogen linking with the addition of water in the two possible directions.



Thus, the amine lies between a hydrocarbon and hydroxylamine on the one hand and an alcohol and ammonia on the other;

the aldimide falls between a β -substituted hydroxylamine and an aldehyde ammonia; the nitrile is related to an aldoxime and an amide, while the nitrile oxide is associated with an isonitro compound and a hydroximic acid.

It will be noted that the compounds represented in Column A of this table have never been made by the hydrolysis of the corresponding transition compounds in Column B; these transition compounds upon hydrolysis always yield substances whose formulas stand opposite them in Column C.

In this connection some of the actual experiments carried out by Bamberger and others are worthy of mention. In a series of articles, Bamberger¹ and his co-workers have presented the results obtained in the oxidation of primary, secondary and tertiary amines with Caro's acid. Ethylamine² upon oxidation gave acetaldoxime, acetonitrile, acetic acid, ammonia, nitroethane and acethydroxamic acid. The first step in the oxidation, β -ethylhydroxylamine, could not be detected. With tertiary butylamine, however, Bamberger and Seligman obtained β -tertiarybutylhydroxylamine, $(\text{CH}_3)_3\text{C.NHOH}$. Benzylamine³ gave benzaldoxime, benzonitrile, benzaldehyde, ammonia, benzamide, benzoic acid, benzhydroxamic acid and phenylnitromethane. In a similar fashion, starting with one of the higher oxidation products, acetaldoxime, Bamberger obtained chiefly nitroethane and acethydroxamic acid. Benzaldoxime⁴ (20.7 grams) gave benzaldehyde (0.3 gram), benzoic acid (7.6 grams), benzamide (trace), phenylnitromethane (2.3 grams), benzhydroxamic acid (2.6 grams) and nitric acid. Bamberger assumed that the first step in the process of oxidation should be represented by the direct addition of oxygen to the nitrogen; this mechanism was proposed because of the ease with which tertiary amines were oxidized to amine oxides, $\text{R}_3\text{N}::\text{O}$.

These experiments show conclusively that during the oxidation of an amine, $\text{R.CH}_2\text{NH}_2$, with Caro's acid, the nitrile is the only one of the three transition compounds actually isolated,

¹ Bamberger and Tschirner: *Ber. d. chem. Ges.*, **31**, 1522 (1898); **33**, 342, 1675 (1899).

² Bamberger: *Ibid.*, **33**, 4293 (1902).

³ Bamberger and Scheutz: *Ibid.*, **34**, 2029, 2262 (1901).

⁴ Bamberger: *Ibid.*, **33**, 1781 (1900).

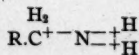
but that the three pairs of related isomers, viz., β -substituted hydroxylamines and aldehyde ammonias, aldoxime and amide, isonitroparaffin and hydroxamic acid, or products formed from them by hydrolysis (aldehydes, acids, ammonia, hydroxylamine) appear in almost every case.

Hydrolysis as a Means of Determining the State of Oxidation of the Nitrogen and the Carbon Atoms.—Since the four transition compounds and the three pairs of corresponding isomers may all be hydrolyzed, it would seem to be permissible to draw conclusions concerning the state of oxidation of the carbon atom and of the nitrogen atom in each one from the products of hydrolysis; at least, such products would indicate the state of oxidation which must have prevailed within the molecule immediately preceding the separation of the carbon atom from the nitrogen atom. In the following discussion, it is proposed to use this principle as a guide to interpret the mechanism of hydrolysis in the case of these various classes of organic compounds, the object being to see whether the electronic conception of valence is of any real assistance as a working hypothesis in these particular cases, and then to apply it in other cases of a similar character to be found at every turn in organic chemistry.

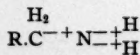
PART I. REACTIONS AMONG CERTAIN CLASSES OF COMPOUNDS CONTAINING NITROGEN

1. *The Relations between Amines, $R.CH_2.NH_2$, and their Products of Hydrolysis*

Amines may be hydrolyzed, but with some difficulty. In every case, however, the nitrogen is eliminated as ammonia, and an alcohol (phenol) forms the second product. In terms of the electronic conception of valence, we are led by these facts to represent the linking between the carbon atom and the nitrogen atom in the amine by electronic formula (I):



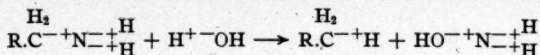
Amine (I)



Amine (II)

The electromere corresponding to Formula II does not seem

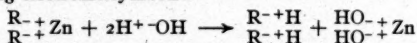
to have a real existence, since such a formula for the amine would demand that the products of hydrolysis be a hydrocarbon on the one hand and hydroxylamine on the other. Thus:



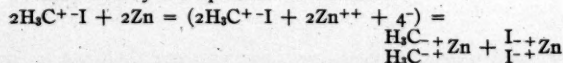
But, as yet, these products have never been found among the substances actually obtained by hydrolyzing the amine.

These considerations would seem to lead to the conclusion that a carbon atom when linked directly to a nitrogen atom does not readily take from it negative electrons, or, in other words, is not readily reduced by it. This conclusion will be strengthened by evidence presented in connection with other classes of compounds discussed later in this article.

The conditions appear to be quite the reverse with certain elements like zinc, magnesium, etc., which form metal-organic compounds. Thus, zinc dialkyls, when hydrolyzed, give hydrocarbons and zinc hydroxide. In view of this fact, the formulas of zinc alkyls and their hydrolysis must be represented by the following electronic symbols:



The synthesis of zinc dimethyl from methyl iodide and zinc, omitting for convenience the intermediate stage R.Zn.I , may be illustrated by the equations which follow:



The electronic formula used for methyl iodide is justified by the fact that methyl iodide yields methyl alcohol and hydrogen iodide upon hydrolysis.¹ If zinc dimethyl were represented by the electronic formula



it should be resolved by hydrolysis into methyl alcohol and zinc hydride; and if the electronic formula were

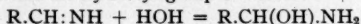


¹ Abegg: Z. anorg. Chem., **39**, 373 (1903).

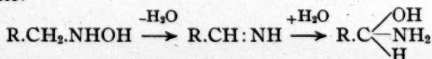
it should yield methane, methyl alcohol and zinc, or by direct dissociation ethane and zinc. Consequently, in the linking $C^+ \cdot Zn$, we must assume a process of oxidation and reduction in which the zinc atom is oxidized and the carbon atom is reduced, or, in terms of the hypothesis, the zinc atom loses two negative electrons which are gained by the carbon atom.

2. *The Relations between Aldimides, β -Alkyl(aryl)hydroxylamines and Aldehyde Ammonias*

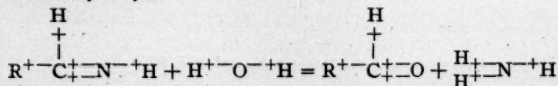
When aldimides, $R.CH : NH$, are hydrolyzed they yield aldehyde ammonias, or ultimately aldehydes and ammonia. This change requires the addition of water to the aldimide and must be represented by formulas in which hydrogen passes to nitrogen and the hydroxyl group to carbon:



It may be imagined, however, that the molecule of water might be added in the reverse direction, viz., hydrogen to carbon and hydroxyl to nitrogen, which would lead to the formation of a β -substituted hydroxylamine. An inspection of the usual formula, $R.CH : NH$, brings to light nothing which would prevent such a theoretical conclusion, and it is only the initiated who can unerringly predict that hydrolysis will lead to the formation of an aldehyde and ammonia by reading into the formula more than it actually contains. In other words, the reactions expressed in the following equations might be reversible:

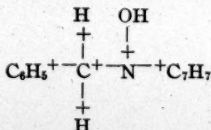


But there is not a single experimental result which substantiates this supposition; aldimides always yield ammonia and an aldehyde, and never by hydrolysis alone β -substituted hydroxylamines. These facts would demand the following electronic formula for aldimides. The equation also represents the process of their hydrolysis:

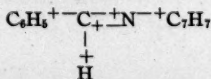


Although β -substituted hydroxylamines and β -disubstituted hydroxylamines are not known to be formed by the hydrolysis of aldimides or of substituted aldimides, $R\cdot CH:N\cdot R$, it has been shown that both classes of compounds in the presence of mild dehydrating agents are converted, probably through aldimides, into aldehydes and ammonia (or amines). It seems plausible, therefore, to assume that this change is brought about by a loss of water between carbon and nitrogen in one direction and an addition of water in the reverse direction in the manner indicated by the equation given above. Thus, Walder¹ found that β -dibenzylhydroxylamine, $(C_7H_7)_2NOH$, with an excess of acetyl chloride gave chiefly benzaldehyde and benzylamine. The same transformation was brought about by treating the compound with acetic acid in which hydrogen chloride was dissolved ("Beckmann's mixture"). Behrend and Leuchs² stated that benzaldehyde and benzylamine were formed by the direct splitting of β -dibenzylhydroxylamine into these two products. In a footnote to Walder's article, Victor Meyer³ spoke of the reaction as an "intramolecular Selbstoxydation."

This reaction presents a number of interesting features when it is considered from the electronic point of view. It is evident that β -dibenzylhydroxylamine must be regarded as a derivative of hydroxylamine and benzyl alcohol:



By a loss of one molecule of water, an electromere of the following formula would be expected:

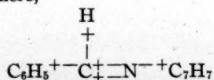


¹ Walder: Ber. d. chem. Ges., **19**, 1629, 3287 (1886).

² Behrend and Leuchs: Ann. Chem. (Liebig), **287**, 233 (1890).

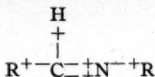
³ Walder: Loc. cit., 1629 (note).

But by hydrolysis alone this electromere could not yield benzylamine and benzaldehyde. It would either regenerate the original β -dibenzylhydroxylamine, or be decomposed into β -monobenzylhydroxylamine and benzyl alcohol. Consequently, before benzylamine and benzaldehyde can be formed there must be an "intramolecular Selbstoxydation" as Victor Meyer called it, or the carbon atom must yield negative electrons which are at once combined with the nitrogen atom to give a new electromere,



This electromere, and this one alone, can explain the formation of benzylamine and benzaldehyde.

Assuming that R and H linked to carbon are both positive,¹ one other electronic formula may be written

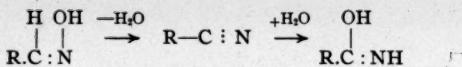


But this formula could not represent the aldimide obtained from β -disubstituted hydroxylamines since, upon hydrolysis, it would yield a hydrocarbon and a derivative of dihydroxylamine (a nitroso compound or an oxime).

3. The Relations between Nitriles, Aldoximes and Amides

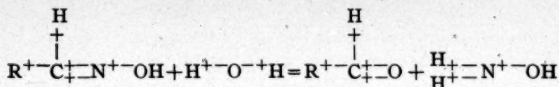
Nitrile I.—Under the influence of reagents which of themselves possess neither oxidizing nor reducing properties, a *syn*-aldoxime loses one molecule of water, and a nitrile is produced. But when water is added to this same nitrile, the resulting compound is always an amide, or finally ammonia and a carboxylic acid, and never the original aldoxime from which the nitrile was obtained by loss of water. These changes are usually represented by structural formulas which show that water is lost by the aldoxime in one direction, and that the amide is formed by the addition of water in the reverse direction to the carbon-nitrogen linking of the nitrile:

¹ If either R or H is negative, or if both R and H are negative, it is evident that other electronic formulas are conceivable.

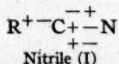


An inspection of this reaction, however, leads to the conclusion that the nitrile, which one might expect from the aldoxime, should be an electromere of the nitrile which yields the amide, and that it could not be identical with it, a conclusion which is suggested in no way whatsoever by the usual structural formula, $\text{R.C} : \text{N}$.

This statement will be evident if one recalls that the aldoxime, when hydrolyzed, gives an aldehyde and hydroxylamine. That is, the carbon-nitrogen linking must be represented by some combination of the symbols $\overset{+}{\text{C}}\text{--}$ and $\text{N}\overset{+}{\text{--}}$. Consequently, the electronic formula of the aldoxime and the course of its hydrolysis may be shown by the following equation:



In view of these relations, it would seem logical to assume that a loss of water by the aldoxime should give, at least transiently, an electromere of the following formula:



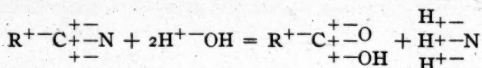
and that a nitrile of this particular formula should regenerate the aldoxime, or, at any rate, when completely hydrolyzed, would give an aldehyde and hydroxylamine.

Nitrile II.—Now, a nitrile which would yield an amide, or ammonia and a carboxylic acid, could result from this electromere (I) by intramolecular oxidation; that is, by an exchange of negative electrons between carbon and nitrogen:



Since all known nitriles, when hydrolyzed, give amides (or am-

monia and carboxylic acids), and never an aldoxime or an aldehyde and hydroxylamine, it is to be inferred that they should be represented by the electronic formula (II). The hydrolysis would then be indicated as follows:



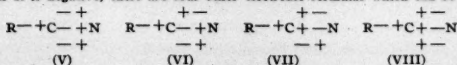
When the radical R is regarded as positive,¹ it is self-evident that in addition to the two nitrile formulas already given, two other electronic formulas are possible, viz.:



A nitrile of Formula (III) by hydrolysis would yield an alcohol and dihydroxylamine (or hyponitrous acid), while one of Formula (IV) would give a hydrocarbon and nitrous acid. Although no nitriles possessing these properties are known, it seems highly probable that they are formed as transition products in certain reactions.

Nitrile III.—Thus, Seliwanow² pointed out the hypochlorous character of chlorine in monochloro- and dichloroamines, RNHCl and RNC₂l, and in nitrogen trichloride, NCl₃. This was made evident by the fact that all of the chlorine in these compounds could be eliminated as hypochlorous acid. Seliwanow determined the amount of iodine liberated by the action of compounds of the formula RNHCl upon an acidulated solution of potassium iodide, and found that, for every atomic weight of chlorine in these compounds, two atomic weights of iodine were liberated. Previous to this time, Schuetzenberger³ had prepared compounds of the type R.C(OC₂l) : O and had suggested that chlorine, in these compounds, played

¹ If R is negative, there are four other electronic formulas which can be written

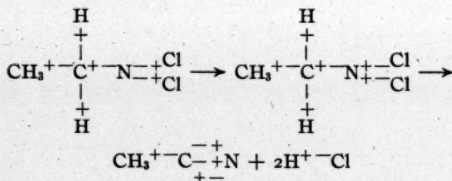


² Seliwanow: Ber. d. chem. Ges., **25**, 3617 (1892). Noyes: J. Am. Chem. Soc., **35**, 767 (1913).

³ Schuetzenberger: Ann. Chem. (Liebig), **120**, 113 (1861).

the role of an electropositive metal in the salts. In terms of the electronic conception of valence, chlorine in all of these compounds must be considered as positive, Cl^+ .¹

By the action of alcoholic potash upon dichloroethylamine, $\text{C}_2\text{H}_5\text{NCl}_2$, Seliwanow obtained potassium acetate, ammonia and potassium chloride. In terms of the present mode of viewing the reaction, the following equation would indicate the course of the reaction:



It will be observed that the nitrile here represented would correspond to nitrile (III) shown above. This nitrile, however, by intramolecular oxidation, must pass at once to the usual electromere (I), $\text{CH}_3^+ - \text{C}^+ - \text{N} \rightarrow \text{CH}_3^+ - \text{C}^+ - \text{N}$, which, in turn, would give the products actually obtained by Seliwanow, viz., acetic acid and ammonia. Similar changes have been observed by Berg² in the study of the chlorine derivatives of secondary amines, $\text{RR}'\text{NCl}$. Thus, ethylamine chloride, $(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_{11})\text{NCl}$, with alkalis gave either acetaldehyde, amylamine and a chloride (KCl), or valeric aldehyde, ethylamine and a chloride. In a previous article,³ I suggested that similar reactions accompany the Beckmann rearrangement of bromo amides according to the Hofmann method.

From these reactions, the conclusion may be drawn that, in alkaline solutions at least, a system $\text{>C}^+ - \text{N} - \text{Cl}$ tends to

¹ Noyes: J. Am. Chem. Soc., **23**, 463 (1901). Stieglitz: *Ibid.*, **23**, 769 (1901); **29**, 51 (1903). Walden: Z. physik. Chem., **43**, 407-43 (1903). J. J. Thompson: The Corpuscular Theory of Matter, p. 130 (1907).

² Berg: Bull. soc. chim., [3] **17**, 297 (1897).

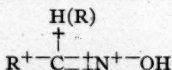
³ Jones: THIS JOURNAL, **48**, 26 (1912).

pass to a system $>\text{C}^{\overset{+}{\text{H}}}-\text{N}^+-\text{Cl}$, which, in turn, by an exchange of negative electrons between carbon atom and the nitrogen atom, with the loss of H^+-Cl , finally becomes $>\text{C}^+=\text{N}$.

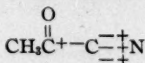
Nitrile IV.—It will be recalled that oximes are frequently prepared by the action of nitrous acid or amyl nitrite upon compounds containing methylene groups, $\text{R}.\text{CH}_2.\text{R}'$, especially when R or R' are so-called negative groups (e. g., $\text{RC}:\text{O}$). Furthermore, certain derivatives of nitrous acid (NOCl , N_2O_3) may be added to olefin hydrocarbons, and to hydrocarbons of the hydroaromatic series. The latter reaction plays a very important role in the study of the terpenes. If the nitroso compounds obtained by the addition of these reagents contain

a grouping $>\text{C}^{\overset{\text{H}}{\diagup}}_{\text{N}:\text{O}}$ in their formulas, a rearrangement may be brought about to give oximes $>\text{C}:\text{NOH}$.

For example, amyl nitrite, in the presence of sodium ethylate, converts acetone into isonitrosoacetone, $\text{CH}_3.\text{CO}.\text{CH}:\text{NOH}$. If reactions of this kind consisted merely in the loss of alcohol or water, whether intermediate products in the nature of addition products are assumed or not, the oximes which would be formed must be assigned the electronic formula

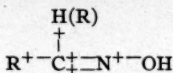


that is, the nitrogen must still be in the state of oxidation which it has in nitrous acid. When isonitrosoacetone, prepared in the manner described above, is treated with acetic anhydride, a nitrile, acetyl cyanide, is formed. Assuming that the electronic formula just given represents the state of oxidation in isonitrosoacetone, acetyl cyanide, which differs from it by one molecule of water, must receive the following electronic formula:

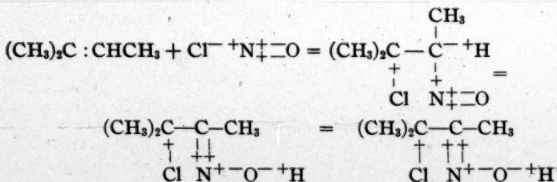


If our reasoning were correct, this nitrile should be a nitrile of Formula (IV) previously indicated.

But oximes prepared by the methods described are not different in chemical behavior from oximes prepared by the action of hydroxylamine upon carbonyl compounds;¹ they all yield hydroxylamine and a carbonyl compound upon hydrolysis, and never nitrous acid accompanied by the original methylene derivative. Furthermore, the nitriles (e. g., acetyl cyanide) obtained from these aldoximes always give ammonia and a carboxylic acid and not nitrous acid which would be demanded if the formula given above were correct. Consequently, all such reactions with nitrous acid must involve not merely a loss of water, but also a simultaneous intramolecular oxidation and reduction in which the carbon atom loses negative electrons, and the final state must be shown by the electronic formula



In a similar manner, the addition of nitrosyl chloride and of nitrous anhydride to unsaturated compounds leads to the formation of oximes by processes of rearrangement and simultaneous intramolecular oxidation. Thus:

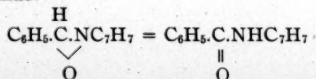


From these considerations it may be inferred that the existence of nitriles of the formulas $\text{R}^+ - \text{C}^+ - \text{N}^+$, or $\text{R}^+ - \text{C}^+ - \text{N}^+$ is highly improbable, and that even if they should occur transiently in reactions similar to those described above, they would

¹ Thus, violuric acid may be prepared by the action of nitrous acid upon malonyl-urea or by the action of hydroxylamine upon mesoxalylurea.

be transformed at once by intramolecular oxidation and reduction into the stable and usual form $R^+-C \equiv N$.

Isoaldoximes.—Beckmann¹ studied the behavior of isoaldoximes. In the presence of acid chlorides, or of hydrogen chloride dissolved in acetic acid ("Beckmann's mixture"), benzylisobenzaldoxime, which gave benzaldehyde and β -benzylhydroxylamine upon hydrolysis, was converted into benzylbenzamide:



It is surprising how easily this change may be accomplished. According to Beckmann, 0.0456 gram of acetyl chloride was sufficient to cause the rearrangement of one gram of benzylisobenzaldoxime. It will be evident that this change must be accompanied by a transfer of electrons between carbon atom and the nitrogen atom, since the isoaldoxime, which yields benzaldehyde and β -benzylhydroxylamine, must be represented by some combination of the symbols $\equiv C^+$ and N^- , while benzylbenzamide, which yields benzylamine and benzoic acid upon hydrolysis, must be represented by the symbols $\equiv C^+$ and N^- .

4. The Relations between Nitrile Oxides, Isonitroparaffins and Hydroxamic Acids

The Conversion of Nitro Compounds into Hydroxamic Acids.

—Shortly after Victor Meyer² announced that nitroparaffins could be prepared by the action of halogen alkyls upon silver nitrite, Preibisch³ observed that primary nitroparaffins heated with concentrated hydrochloric acid gave fatty acids and hydroxylamine. At that time, this reaction was considered very remarkable; for it was not apparent how the hydrolysis of a nitro compound, a derivative of nitrous acid, could give hydroxylamine.

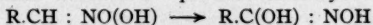
¹ Beckmann: Ber. d. chem. Ges., **26**, 2272 (1893).

² V. Meyer: Ann. Chem. (Liebig), **171**, 19 (1872).

³ Preibisch: J. prakt. Chem., [2] **7**, 480 (1873); **8**, 316 (1874). V. Meyer and Locher: Ann. Chem. (Liebig), **180**, 163 (1876).

Somewhat later, Nef¹ found that a solution of sodium isonitromethane, when mixed with mercuric chloride, gave some mercuric fulminate. Since the study of the fulminates had induced him to look upon fulminic acid as carbon monoxide oxime, $\text{HON} : \text{C}$, a derivative of bivalent carbon, here again was a case in which a nitro compound, by comparatively simple chemical reactions, had been converted into a derivative of hydroxylamine.

Jones² advanced the view that the formation of hydroxylamine and fatty acid, as well as the conversion of isonitromethane into fulminate, had a common cause, viz., the preliminary transformation of the isonitroparaffin into a hydroximic acid:

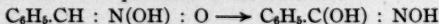


Support was given to this interpretation by the singular behavior of the primary isonitroparaffin salts towards acid chlorides. Jones³ found that sodium isonitroethane, $\text{CH}_3\text{CH} : \text{N}(\text{ONa}) : \text{O}$, reacted with benzoyl chloride but that the benzoyl ester of the isonitroparaffin could not be obtained; in its stead, the benzoyl ester of acethydroxamic acid was formed.



This reaction was described as a case of intramolecular oxidation, and the intimate relation existing between isonitro compounds and hydroxamic acids was dwelt upon in the interpretation.

Subsequently, this interrelation was brought out more emphatically by Bamberger⁴ who observed that hydroxamic acids were formed in small amounts when solutions of the salts of certain primary isonitro compounds were poured into dilute mineral acids. Later, Bamberger⁵ brought about the change directly by heating phenylnitromethane with sulphuric acid, and was able to prove that benzhydroxamic acid was one of the products of the reaction:



¹ Nef: *Ann. Chem. (Liebig)*, **280**, 275 (1894).

² Jones: *THIS JOURNAL*, **30**, 35 (1898).

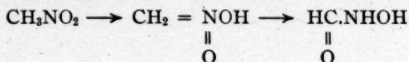
³ Jones: *Loc. cit.*, p. 2. Van Raalte: *Rec. trav. chim.*, **18**, 378 (1899).

⁴ Bamberger and Rust: *Ber. d. chem. Ges.*, **35**, 47 (1902).

⁵ Bamberger: *Loc. cit.*, p. 52. Cazeneuve: *Compt. rend.*, **190**, 244.

In the case of *p*-nitrophenylnitromethane, heated to 130° with sulphuric acid (65 parts concentrated acid to 100 parts of water), he isolated *p*-nitrobenzhydroxamic acid in considerable amount without any difficulty. Furthermore, it may be recalled that Bamberger found both nitro compounds and hydroxamic acids among the products which resulted when primary amines were oxidized with Caro's acid (p. 418).

The surprising ease with which, at times, this transformation may occur is strikingly illustrated by an observation recently reported by Angeli¹ who found that nitromethane itself, when exposed to light, first showed a change to isonitromethane, and that later small amounts of formhydroxamic acid could be shown to be present:



Nitrile Oxides.—By the action of sodium carbonate upon chlorobenzhydroximic acid, $\text{C}_6\text{H}_5\cdot\text{CCl}:\text{NOH}$, Werner and Buss² prepared benzonitrile oxide. The monomolecular form, to which they assigned the formula $\text{C}_6\text{H}_5\cdot\text{C}:\text{N}:\text{O}$, was not isolated by them, but only a dimolecular polymer which they considered to be diphenylglyoxime peroxide. Later, by a more careful treatment of chlorobenzhydroximic acid with sodium carbonate, Wieland³ obtained benzonitrile oxide in its monomolecular form as a solid melting at 15°. It showed a remarkable tendency to polymerize, and gave not only two dimolecular polymers, diphenylfuroxan and dibenzoxoazoxime, but also a trimolecular form.

Benzonitrile oxide, when reduced, gave benzonitrile, but, strange to say, an attempt to prepare the nitrile oxide by the oxidation of benzonitrile with Caro's acid failed. When either the monomolecular form or its polymers were heated with indifferent solvents (benzene, toluene) they were changed into phenyl isocyanate. Because of the failure of the nitrile oxide to react by addition with ammonia, aniline, bromine,

¹ Angeli: Ber. d. chem. Ges., **45**, 1775 (1912).

² Werner and Buss: Ber. d. chem. Ges., **27**, 2199 (1894).

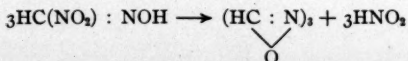
³ Wieland: *Ibid.*, **40**, 418 (1907); **43**, 803 (1909).

etc., Wieland¹ preferred the formula $C_4H_5.C : N$ to the one

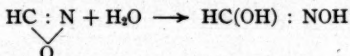


proposed by Werner and Buss, but the evidence does not seem to be altogether convincing.

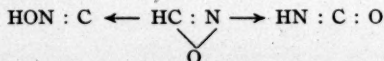
By the action of sodium carbonate upon methylnitrolic acid, Wieland succeeded in making the simplest nitrile oxide, formonitrile oxide, but only in a trimolecular form, a yellow explosive solid which he called trifulmine:



The hydrolysis of trifulmine presents many interesting features. With acids, hydroxylamine salts and formic acid were produced. Concentrated hydrochloric acid gave considerable formyl chloride oxime ($HON : CHCl$), through which trifulmine could be converted into silver fulminate (Nef).² If water alone was used, the chief product was *formhydroxamic acid*,



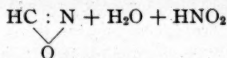
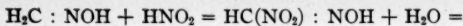
while alkalis gave isocyanate (or carbonate and ammonia). Wieland pointed out that formonitrile oxide might be expected to yield either fulminic acid or isocyanic acid since it is isomeric with these two substances:



There is no mention, however, in Wieland's articles of the conversion of formonitrile oxide into isonitromethane by the addition of water, a change which would not seem to be altogether improbable in view of the fact that methylnitrolic acid, the source of trifulmine, is prepared by the action of nitrous acid upon isonitromethane:

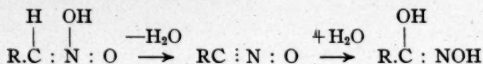
¹ Ber. d. chem. Ges., **40**, 1669 (1907).

² Nef: Ann. Chem. (Liebig), **320**, 310 (1894).

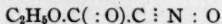


A superficial inspection of these equations would lead to the conclusion that the net result of the reactions is a loss of one molecule of water by the isonitromethane, since HNO_2 in the first equation and in the last equation would cancel.

The nitrile oxides, therefore, seem to form transition compounds which may be placed between the isonitro compound and the hydroximic acid in much the same way that nitriles lie between aldoximes and amides:



In the light of Wieland's recent experiments, it seems highly probable that careful experimentation would lead to the direct preparation of nitrile oxides from primary isonitro compounds by processes of dehydration similar to those employed in making nitriles from aldoximes. In fact, several year ago, Hantzsch¹ subjected phenylisonitromethane, $\text{C}_6\text{H}_5\text{CH} : \text{N}(:\text{O})\text{OH}$, to the action of phosphorus pentachloride and of phenyl isocyanate. Violent reactions occurred in both cases; treatment with phenyl isocyanate gave *diphenylurea* and oily products which he did not succeed in resolving into pure substances. In the literature, I have found only one instance of the direct conversion of a nitro compound into a nitrile oxide. When silver nitrite reacts with ethyl monobromoacetate, no ethyl nitroacetate was produced. In its place, a compound differing from it by one molecule of water was obtained to which Scholl and Schoefer² assigned the formula

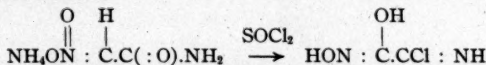


It was accompanied by a dimolecular form. Both of these compounds when reduced gave glycocoll. Here would seem to be a case in which a nitro compound, by loss of water, had

¹ Hantzsch: Ber. d. chem. Ges., **33**, 614, 620 (1899).

² Scholl and Schoefer: *Ibid.*, **34**, 870 (1901).

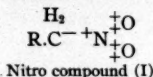
passed directly into a nitrile oxide. Recently, Steinkopf¹ has prepared nitroacetic acid and some of its derivatives. He found that the ammonium salt of nitroacetamide in the presence of thionyl chloride, even at 50°, was converted into β -oximinooxalimino chloride, a hydroximic acid derivative of oxalic acid:



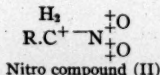
Electronic Formulas of Nitroparaffins and Isonitroparaffins.—

There are two important methods of making nitro compounds, viz., by the action of nitric acid upon hydrocarbons, and by the action of a nitrite upon halogen alkyls (aryls).

The preparation of nitro derivatives by the direct nitration of hydrocarbons with loss of water would point to the formation of compounds in which the nitrogen atom might be assumed to persist in the state of oxidation which it had in nitric acid.² If this were so, the primary nitro compound would have the following electronic formula:



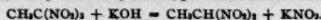
On the other hand, their formation from halogen compounds and nitrites would suggest a formula in which the nitrogen still has the state of oxidation corresponding to that in nitrous acid:



Direct hydrolysis does not lead to a choice between these two electromeres, for primary nitro compounds obtained from either source give chiefly hydroxylamine and a carboxylic acid, and not nitric acid or nitrous acid accompanied by a hydrocarbon or an alcohol. Since, however, the primary nitro compounds

¹ Steinkopf: J. prakt. Chem., **81**, 97, 193.

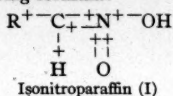
² It is interesting to note that Hantzsch (Ber. d. chem. Ges., **32**, 637 (1899)) found that trinitroethane, with potassium hydroxide, gave dinitroethane and potassium nitrate:



obtained by the two processes are identical, Formula (II) seems the more plausible; and from previous results described in this paper it may be concluded that an electromere of Formula (I) would tend to pass into one of Formula (II) by an exchange of negative electrons between the carbon atom and the nitrogen atom:



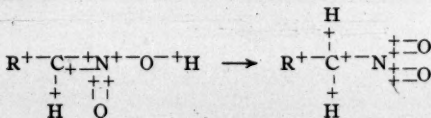
Isonitro Compounds.—Primary nitro compounds prepared by either method are changed into salts of isonitro compounds by the action of alkalis or sodium ethylate. Provided this change is a rearrangement pure and simple, the isonitro compound obtained from the nitro compound of formula (II) would have the following formula:



This conclusion seems to be verified by experiments with salts of the isonitro compounds. It is a well-known fact that very careful treatment of solutions of isonitroparaffin salts with exactly one equivalent of acid leads to the separation of the *aci*-nitroparaffin,¹ which in turn reverts to the nitro compound itself:

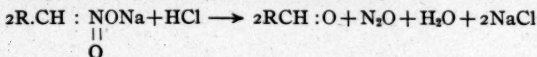


In some cases both the *aci*-form and the nitro compound have been isolated as solids. The *aci*-form is always labile and passes more or less readily into the stable nitro compound. Formula (I) assigned to the isonitro compounds easily explains these changes:



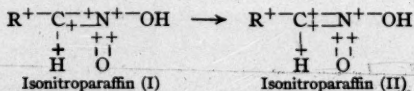
¹ V. Meyer: Ber. d. chem. Ges., **27**, 31, 56 (1894); **28**, 202 (1895). Nef: Ann. Chem. (Liebig), **280**, 266 (1894); Ber. d. chem. Ges., **29**, 1223 (1896). Hantzsch: *Ibid.*, **33**, 613 (1899).

When, however, an excess of acid was used in acidifying the solution of the salt of the isonitro compound, very different results were obtained. Nef¹ showed that salts of primary isonitroparaffins, when treated with an excess of dilute mineral acid, gave chiefly nitrous oxide and an aldehyde:



In addition to these products, he found only traces of nitrous acid, with some fatty acid and hydroxylamine, the latter formed probably by the hydrolysis of the hydroxamic acid, which Bamberger² has shown to be one of the products of these reactions. The mercuric chloride salt of isonitroethane, $\text{C}_2\text{H}_5\text{NO}_2 \cdot \text{HgCl}$, with an excess of acid, gave as much as 98 per cent. of the amount of nitrous oxide calculated.³ Sodium isonitroethane according to Nef⁴ gave 89.4 per cent. of the calculated amount of nitrous oxide. The striking difference in behavior when an exact equivalent of acid was used is shown by experiments reported by Hantzsch,⁵ who succeeded in regenerating nitroethane to the extent of nearly 100 per cent. when great care was taken to avoid excess of acid and to maintain a low temperature.

The conclusions to be drawn from these experiments must be that Formula (I) assigned to isonitroparaffins cannot represent the isonitroparaffin as it participates in this reaction; that is to say, it could not explain the formation of aldehyde and nitrous oxide, since the carbon-nitrogen linking in Formula (I) corresponds to alcohol and nitrous acid. Therefore, in the presence of an excess of acid, isonitroparaffin (I) must change to a second electromere:



¹ Nef: *Loc. cit.*, p. 266.

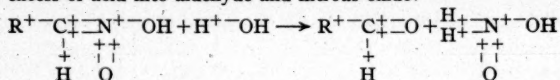
² Bamberger and Rust: *Ber. d. chem. Ges.*, **35**, 47 (1902).

³ Nef: *Ann. Chem. (Liebig)*, **330**, 272 (1894).

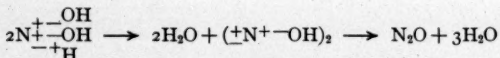
⁴ Nef: *Loc. cit.*, p. 268.

⁵ Hantzsch and Veit: *Ber. d. chem. Ges.*, **32**, 618 (1899).

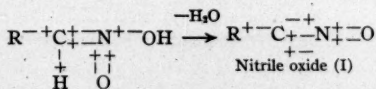
An electromere having this formula (II) would explain the decomposition of the salts of primary isonitroparaffins by an excess of acid into aldehyde and nitrous oxide:



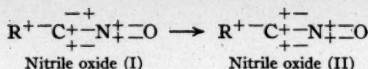
By rearrangement, this form, $\text{H}_2\text{N}(\text{OH}) : \text{O}$, would give dihydroxylamine, then hyponitrous acid, and finally nitrous oxide and water:



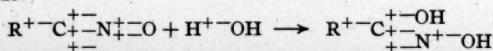
Isonitro Compounds and Hydroxamic Acids.—The fact that in all of these reactions small amounts of hydroxamic acids make their appearance, and that certain primary nitro compounds by the action of moderately concentrated sulphuric acid may be changed into hydroxamic acids, demands an explanation. The assumption has already been made (p. 433) that nitrile oxides form the intermediate products in this transformation in much the same way that aldimides and nitriles may be regarded as intermediate stages in the transformation of β -substituted hydroxylamines and aldoximes into aldehyde ammonias and amides. The conditions met with here are very similar to those discussed in the previous cases. That is to say, the nitrile oxide formed from an isonitro compound of Formula (II) cannot be the nitrile oxide which gives a hydroxamic acid by the addition of water, but must be an electromere of it:



A nitrile oxide of this formula (I) would be hydrolyzed to give an aldehyde and nitrous oxide. Therefore, before a hydroxamic acid can be formed, there must be an exchange of electrons between the carbon atom and the nitrogen atom, and a second electromere must result:



This conclusion is justified by the fact that all nitrile oxides, as well as all hydroxamic acids, when hydrolyzed, give hydroxylamine and a carboxylic acid. The readiness with which nitrile oxides yield hydroxamic acids is emphasized by the experiments of Wieland¹ with formonitrile oxide and aceonitrile oxide:



Summing up all of these changes, we see that, in the case of the primary nitroparaffins, the state of oxidation of the carbon atom and of the nitrogen atom linked together tends to pass from the system $\equiv \text{C} \equiv$ and $\text{N} \equiv$ to a system $\overset{+}{\underset{+}{\text{C}}} \equiv$ and $\text{N} \equiv$; that is, to substances which are hydrolyzed to give a carboxylic acid and hydroxylamine. These observations would seem to justify the assumption previously made that a carbon atom when linked directly to a nitrogen atom does not readily take from it negative electrons or, in other words, is not readily reduced by it.

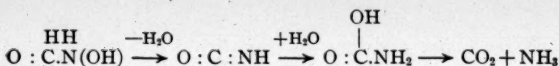
5. The Relations between Hydroxamic Acids, Isocyanates and Carbamic Acids

At least one more transition is possible, viz., a change which would give a system in which the carbon-nitrogen linking would contain carbon in a state of oxidation corresponding to that which it has in carbonic acid ($\overset{+}{\underset{+}{\text{C}}} \equiv$) and nitrogen in a state of reduction corresponding to that which it has in ammonia ($\text{N} \equiv$).

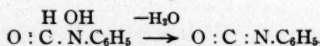
Such a transformation is nicely illustrated by formhydroxamic acid which, in the presence of alkalis, gives isocyanates, carbamates, or carbonates and ammonia.²

¹ Wieland: *Loc. cit.*

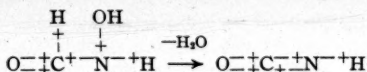
² Wieland: *Die Knallsäure*, p. 32 (1909).



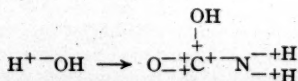
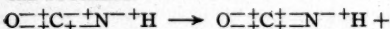
Biddle¹ found that the sodium salt and the lead salt of form-hydroxamic acid could not be kept because they passed spontaneously into carbonates and ammonia. Bamberger and Destraz² subjected N-formylphenylhydroxylamine to the action of dehydrating agents (phosphorus pentoxide) and obtained phenyl isocyanate as one of the products of the action:



If this change is assumed to proceed in a manner similar to those described in previous cases, that is, if the hydroxamic acid loses one molecule of water,³ the isocyanate produced could not yield a carbamate or carbonate and ammonia without previous intramolecular oxidation, or exchange of electrons.



The electromere here represented must pass to a second electromere before carbamic acid or carbonic acid and ammonia can be formed:

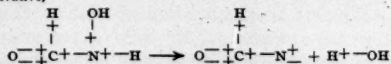


Nitromethane, therefore, presents a very simple illustration

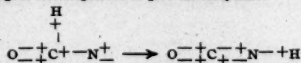
¹ Biddle: *Ann. Chem. (Liebig)*, **310**, 15 (1899).

² Bamberger and Destraz: *Ber. d. chem. Ges.*, **34**, 243 (1901); **35**, 1883 (1902).

³ It may be assumed that a loss of one molecule of water yields first a univalent nitrogen derivative,



and that this undergoes rearrangement to give the isocyanate



of the changes brought about by successive steps in the process of intramolecular oxidation and reduction. The initial and final stages may be summed up in a single equation:



Therefore, starting with the carbon atom in the condition represented by the electronic symbol $\equiv\text{C}^+$ (or possibly $\equiv\text{C}^-$), the entire gamut of oxidation has been traversed, ending with the carbon atom in the condition shown by the symbol $\dagger\text{C}^\dagger$, while, at the same time, the nitrogen atom has suffered reduc-

tion from the condition indicated by the symbol $\text{N}^{\dagger\dagger}$ (or possibly

$\text{N}^{\dagger\dagger}$) to the state represented by the symbol $\text{N}^{\dagger-}$.

PART II. THE BECKMANN REARRANGEMENT

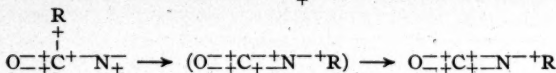
Now, the final stage in the change, viz., the change of form-hydroxamic acid into isocyanic acid, is commonly classed among the Beckmann rearrangements. In my opinion, however, it is not essentially different in mechanism from any of the other changes which preceded it in the series. They all have, in common, intramolecular oxidation and reduction, or an exchange of negative electrons between the carbon atom and the nitrogen atom. In fact, if all of the reactions classed as examples of the Beckmann rearrangement (including the Hofmann and Curtius reactions) are inspected it will be observed that *in every case the rearrangement is accompanied by a process of intramolecular oxidation and reduction*. It seems very probable that this tendency of the system of linking carbon-nitrogen to pass to one in which the carbon atom is as fully oxidized as possible and the nitrogen atom as fully reduced as possible may be the real determining factor in the Beckmann rearrangement, and that the formation of univalent nitrogen, proposed by Stieglitz¹ as the immediate cause, may be a mere incident, necessary, to be sure, to pave the way for this change.

¹ Stieglitz: *THIS JOURNAL*, **18**, 751 (1896); **28**, 49 (1903). Stieglitz and Earl: *Ibid.*, **30**, 399, 412 (1903). Stieglitz and Slossen: *Ber. d. chem. Ges.*, **28**, 3266 (1896); **34**, 1613 (1902). Slossen: *THIS JOURNAL*, **29**, 289 (1903). Jones: *Ibid.*, **48**, 1 (1912).

Univalent nitrogen may be represented by two electronic symbols:



In either case the two auxiliary valences (see p. 416) must be considered the one as positive (+) and the other as negative (−), since the loss of two groups from trivalent nitrogen necessitates that one be positive and the other negative. In the interpretation of the Beckmann rearrangement here proposed, this becomes a very significant fact. One of the free valences of univalent nitrogen must be positive (+) in order that the carbon atom may be oxidized, that is, may lose negative electrons; and the other valence of univalent nitrogen must be negative (−) to receive the positive radical (R⁺) which can no longer remain attached to the carbon atom when all of its valences have become positive (C^+). E. g.:



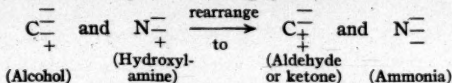
Stieglitz¹ claims that the rearrangement is induced by the "potency of the free valences of univalent nitrogen." The present mode of viewing the rearrangement would speak rather of the "potency" of the carbon atom to lose negative electrons and of the nitrogen atom to acquire them, and would look upon the free valences of univalent nitrogen as the stage setting required to furnish a suitable environment in which the essential action may take place.

The following classes of compounds include those usually discussed in connection with the Beckmann rearrangement: β -monosubstituted hydroxylamines, RNHOH; bromoamines, RNHBr; aliphyl azides, R.CH₂.N₃; aldioximes, RCH:NOH; ketoximes, RRC:NOH; hydroxamic acids RC(:O).N(OH)H and their mono- and diacyl derivatives; alkyl esters of hydroxamic acids, RC(OR):NOH; amidoximes, RC(NH)₂:NOH; acid azides, RC(:O).N₃; and monohalogen amides, RC(:O).N(hal)H. The view of the Beckmann rearrangement presented above would lead naturally to a classification

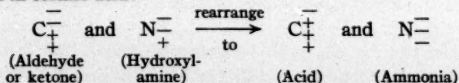
¹ Stieglitz: *Loc. cit.*

of organic compounds into groups determined by the state of oxidation which the carbon atom attached to nitrogen shows preceding and subsequent to the rearrangement. It will be pointed out that in all of these types of compounds, including the monohalogen amines, the monohalogen amides and the azides, the nitrogen atom is actually or potentially¹ in a state of oxidation corresponding to that which it has in hydroxylamine, and that it passes during rearrangement to a state of oxidation comparable to that which nitrogen has in ammonia. In accordance with these principles there would be three distinct groups:

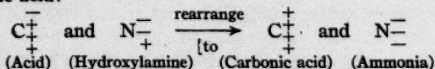
Group I.—Compounds in which the carbon atom of the carbon-nitrogen linking may be regarded as having the state of oxidation shown by the carbon atom in methyl alcohol. During rearrangement the state of oxidation is changed to that shown by the carbon atom in formaldehyde. These changes may be illustrated by the following symbols:



Group II.—Compounds in which the carbon atom of the carbon-nitrogen linking is in a state of oxidation corresponding to that of the carbon atom in formaldehyde. By rearrangement it passes to a state of oxidation comparable to that of the carbon atom in formic acid:



Group III.—Compounds in which the carbon atom of the carbon-nitrogen linking is in a state of oxidation shown by the carbon atom in formic acid. By rearrangement the state of oxidation changes to that shown by the carbon atom in carbonic acid:



¹ Jones: *THIS JOURNAL*, **48**, 26 (1912).

Group I would include azides, such as benzyl azide,¹ $C_6H_5.CH_2.N_3$; monosubstituted hydroxylamines, such as triphenylmethylhydroxylamine,² $(C_6H_5)_3C.N(OH)H$; and monobromo amines, such as triphenylamine bromide,³ $(C_6H_5)_3C.NH(Br)$. Group II would include aldoximes and ketoximes. Group III would include hydroxamic acids, together with their salts and esters, amidoximes, acid azides and monohalogenamides.⁴

Much speculation has been indulged in to explain the manner in which the radical, R, attached to the carbon atom "wanders" to the nitrogen atom. Apart from the plain proposal that the radical, as a whole, changes its position without any complicated mechanism, several hypotheses, involving a change in the character of the radical, have been advanced, but none has satisfied the demands placed upon it by experiment. Hesse⁵ showed that intermediate trimethylene rings could not be assumed since trimethylacetbromoamide, $(CH_3)_3CONHBr$, gave tertiary butylamine by rearrangement, while the assumption of the intermediate formation of a trimethylene ring would require isobutylamine. Nef proposed that the dissociation into bivalent carbon radicals might precede the rearrangement. The evidence for and against this view has been presented by Stieglitz.⁶ At present it cannot be regarded as a satisfactory interpretation. It must be admitted, therefore, that we have no satisfactory mechanism in terms of which to represent the "wandering" of the radical from the carbon atom to the nitrogen atom. The difficulties met with in the rearrangement of stereoisomers are also awaiting explanation. Work is now in progress in this laboratory which promises to throw new light upon these phases of the Beckmann rearrangement.

UNIVERSITY OF CINCINNATI
November 11, 1913

¹ Curtius: J. prakt. Chem., [2] 50, 289; Ber. d. chem. Ges., 27, 778 (1895).

² Stieglitz and Leech: Ber. d. chem. Ges., 46, 2147 (1913).

³ Stieglitz and Vosburgh: *Ibid.*, 46, 2151 (1913).

⁴ Jones: *THIS JOURNAL*, 48, 26 (1912).

⁵ Stieglitz: *Ibid.*, 29, 56 (1903).

⁶ Stieglitz: *Ibid.*, p. 57.

[Contribution from the Chemical Laboratory of the University of Cincinnati]

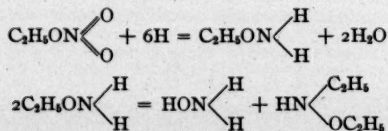
A STUDY OF SOME NEW ALKYLHYDROXYLAMINES

BY CHARLES H. HECKER

The amines have never ceased to be a center of interest since the time of their discovery by Wurtz in 1848. Although substituted hydroxylamines are nearer akin to amines than to any other class of organic compounds, they have shared only to a very minor degree in the attention paid to organic derivatives of nitrogen. Still, in many ways, the questions raised by a deductive consideration of their chemical relations are somewhat more varied and interesting than those presented by amines themselves. The present study, carried out under the direction of Dr. Lauder W. Jones, had, for its main object, the finding of methods whereby the various alkyl derivatives of hydroxylamine may be prepared in sufficient quantities and with a degree of readiness to permit of their future investigation from many other angles. Preliminary arrangements have already been made to study the electrical conductivities of water solutions of the alkylhydroxylamines described in this article.

HISTORICAL

The first representative of the alkylhydroxylamines¹ was described in 1868 by Lossen,² the discoverer of hydroxylamine itself. He found that one of the products of the reduction of ethyl nitrate by tin and hydrochloric acid was a base having the formula $C_4H_{11}ON$. Its properties showed that it was related to hydroxylamine, and he concluded that it was ethoxyethylamine, assuming that the following reactions took place:



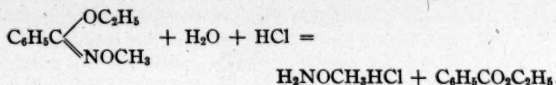
¹ Vorländer: J. prakt. Chem., N. F., 59, 247-8. Throughout this paper the terms "alkyl" and "alanyl" are used interchangeably.

² Lossen: Ann. Chem. (Liebig), Suppl. 6, 238.

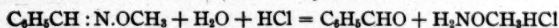
Later, however, Lossen¹ showed that this compound was not ethoxyethylamine, neither is it identical with β -diethylhydroxylamine. Its constitution is doubtful.

No further study of either hydroxylamine or its derivatives was made until, in 1875, Lossen endeavored to justify the formula of hydroxylamine ($\text{HON} \begin{smallmatrix} \text{H} \\ \diagup \diagdown \\ \text{H} \end{smallmatrix}$), which had been criticized, by showing that two of the hydrogen atoms were equivalent, while the third was not. To do this, he replaced these hydrogen atoms by different groups, principally acyl groups.

The next year, Lossen and Zanni² prepared the hydrochloride of α -methylhydroxylamine by hydrolyzing the methyl ester of ethylbenzhydroxamic acid, as shown by the equation



but they did not isolate the alkylhydroxylamine itself. Petraczek³ obtained the same substance by hydrolyzing methylbenzaldoxime with concentrated hydrochloric acid:



Jones⁴ also obtained this substance by hydrolyzing the α -methyl ester of carbethoxyhydroxamic acid with hydrochloric acid.

Lossen and Zanni made α -ethylhydroxylamine by a hydrolysis similar to that given above. Later Waldstein⁵ prepared it from benzhydroxamic ethyl ester by heating this substance with an excess of hydrochloric acid in a sealed tube. Jones⁶ obtained the hydrochloride by treating the reaction product of phosphorus pentachloride and carbethoxyhydroxamic ethyl ester with water, making this solution strongly alkaline with sodium hydroxide and distilling the hydroxylamine into dilute hydrochloric acid. This method gives almost theoretical

¹ Lossen: *Ann. Chem. (Liebig)*, **353**, 234.

² Lossen and Zanni: *Ibid.*, **183**, 225f.

³ Petraczek: *Ber. d. chem. Ges.*, **10**, 827.

⁴ Jones: *THIS JOURNAL*, **30**, 41ff.

⁵ Waldstein: *Ann. Chem. (Liebig)*, **181**, 390

⁶ Jones: *THIS JOURNAL*, **30**, 41ff.

yields. α,β -Dimethylhydroxylamine and α,β -diethylhydroxylamine,¹ also α -methyl- β -ethylhydroxylamine and α -ethyl- β -methylhydroxylamine,² were obtained by Jones by hydrolyzing the respective esters of carbethoxyhydroxamic acid. Lossen had previously obtained the diethylhydroxylamine by alkylating α -ethylhydroxylamine with ethyl bromide.³

In 1888, Bewad⁴ thought that he had made triethylamine oxide $(C_2H_5)_3NO$, by the action of nitroethane upon zinc ethyl, but this compound was shown later⁵ to be β -ethyl- β -sec.-butylhydroxylamine. This synthesis furnishes an easy way of preparing mixed β,β -dialkylhydroxylamines, and was extensively studied by Bewad.⁶

In 1890, Behrend and Leuchs⁷ published a résumé of the work done on the alkyl derivatives of hydroxylamine up to that time, and presented the results of their own investigations in that field, covering the benzyl and ethyl derivatives. Nine years later Dunstan and Goulding⁸ in England, and Mamlock and Wolfenstein⁹ in Germany, by the oxidation of di- and trisubstituted amines with hydrogen peroxide obtained a number of β -dialkylhydroxylamines and the so-called oxamines, or hydroxyamine oxides, compounds isomeric with the trialkylhydroxylamines.

Summing up, we see that up to the present time there is only a single representative of the α -monoalkylhydroxylamines known, for although Lossen and Zanni obtained the hydrochloride of α -methylhydroxylamine, they did not isolate the base. There is a similar paucity of data on the α,β -dialkylhydroxylamines, only two compounds containing like groups and two compounds containing unlike groups being known.

In the present paper are described two new α -monoalkylhydroxylamines, six new α,β -dialkylhydroxylamines, and the intermediate products in their preparation, many of which

¹ Jones: THIS JOURNAL, **30**, 41ff.

² Jones: *Ibid.*, **30**, 253ff.

³ Lossen: Ann. Chem. (Liebig), **252**, 234.

⁴ Bewad: Ber. d. chem. Ges., **21**, Ref. 479.

⁵ Bewad: J. Russ. Phys. Chem. Soc., **32**, 455.

⁶ Bewad: J. prakt. Chem., N. F., **63**, 94ff. and 193ff.

⁷ Behrend and Leuchs: Ann. Chem. (Liebig), **287**, 203ff.

⁸ Dunstan and Goulding: J. Chem. Soc., **75**, 799ff., 1004ff.

⁹ Mamlock and Wolfenstein: Ber. d. chem. Ges., **23**, 159.

are new. Four of these dialkylhydroxylamines are isomeric with each other and with the β,β -ethylpropylhydroxylamine described by Bewad. It is intended to study all of these compounds and others, including the sixth isomer, β -ethyl- β -isopropylhydroxylamine, yet to be made, from the standpoint of their electrical conductivities in water solution.

The method suggested by Jones¹ of introducing successively into hydroxyurethan two different alkyl groups and subsequently hydrolyzing the resulting product was followed in the preparation of the α,β -dialkylhydroxylamines. An alcoholic solution of hydroxyurethan mixed with the theoretical amount of alkyl halide was treated with the calculated amount of an alcoholic solution of potassium hydroxide. This formed a mixture of the mono- and dialkyl esters of carbethoxyhydroxamic acid. One might expect that some of the oxygen ester ($C_2H_5O.C(OR) : NOR$) would be formed at the same time, but none was observed. These two substances were then separated by shaking the ether solution with dilute alkali. By this treatment, the monoalkyl derivative was converted into its salt, which dissolved in the water, while the dialkyl derivative, having no acid properties, remained dissolved in the ether. The alkali salt of the monoalkyl-oxyurethan was easily decomposed by dilute acids to give the free ester, which was extracted with ether, and then obtained in the free state by fractional distillation.

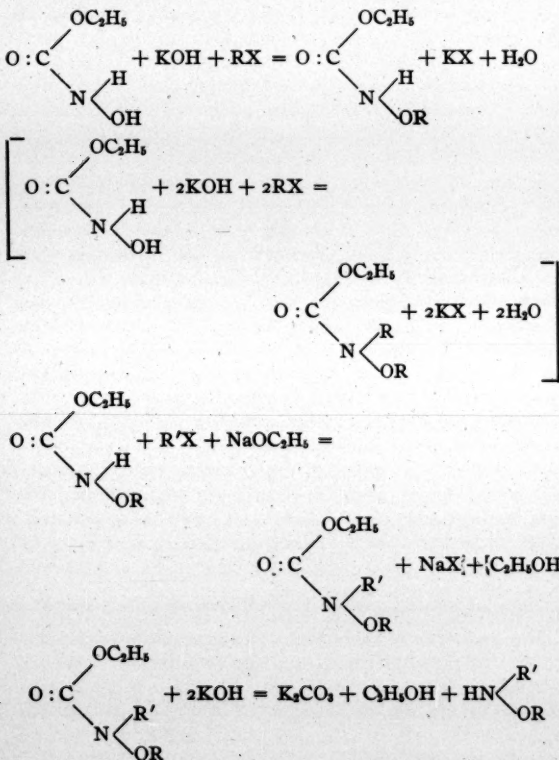
When a mixed α,β -dialkylhydroxylamine was to be made, a mixture of one mole of monoalkylcarbethoxyhydroxamic ester and one mole of alkyl halide was treated with the calculated amount of sodium ethylate dissolved in alcohol. After the dialkyl ester was extracted with ether, it was shaken with dilute alkali to remove any unchanged monoalkyl ester, then dried and fractionated.

The hydrolysis of these esters was accomplished uniformly by heating the ester with a considerable excess of potassium hydroxide solution in a sealed tube for fifteen to sixty hours at temperatures varying from 100° to 200°. To separate the hydroxylamine, the mixture from the hydrolysis was distilled

¹ Jones: *THIS JOURNAL*, **38**, 253ff.

and the free base collected in dilute hydrochloric acid. The hydrochloride formed was recrystallized, decomposed with potassium hydroxide and the vapors of the free alkylhydroxylamine condensed.

The above method may be summarized in the following equations:

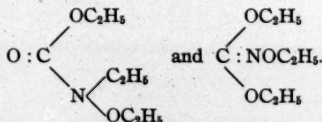


Concentrated hydrochloric acid was tried as the hydrolyzing agent, but gave poor yields of a very impure salt. The α -monoalkyl esters were easily hydrolyzed by the potassium hydroxide solution, but the dialkyl esters with two like groups were decomposed much more slowly. Furthermore, the ease with which the α -monoalkyl esters were hydrolyzed seemed to increase with increasing molecular weight. This is probably partly responsible for the low yields obtained in making the α -monoalkyl esters of carbethoxyhydroxamic acid.

EXPERIMENTAL PART

Action of Ethyl Iodide on the Potassium Salt of Carbethoxyhydroxamic Acid

The carbethoxyhydroxamic acid, which served as the starting point in the preparation of the following compounds, was prepared according to Jones's modification of Hantzsch's method.¹ This was then converted into the ethyl ester by treatment with ethyl iodide and potassium hydroxide,² and the mono- and di-esters separated as described above. The monoethyl ester was used in the preparation of mixed dialkyl-carbethoxyhydroxamic esters. The ether solution of the diethyl ester was dried with anhydrous sodium sulphate and the ether was removed by distillation, under diminished pressure. The oil which was left was impure, as was that obtained by Jones. It was, therefore, fractionated, and two approximately equal fractions, one boiling at 107° to 112° (70 mm. pressure) and the other boiling at 129° to 133° (70 mm. pressure) were obtained. It was at first thought that these two fractions might be two tautomeric forms, viz.:



This could, of course, be determined easily, for the first should give α -diethylhydroxylamine on hydrolysis with potassium

¹ Jones: THIS JOURNAL, 20, 41ff.

² *Ibid.*

hydroxide, while the second should give α -monoethylhydroxylamine. However, the nature of the impurity was determined without this step. An analysis of the higher boiling fraction gave the following results:

0.3987 gram gave 39.2 cc. N_2 at 21° and 747.8 mm. (uncorr.).

	Calc. for α -diethyl- oxyurethan $C_7H_{15}O_2N$	Calc. for α -mono- ethyloxyurethan $C_6H_{11}O_2N$	Found
N	8.69	10.52	10.95

The boiling point of this fraction was found to be 194° to 196° under 750 mm. pressure. The boiling point of α -monoethylcarbethoxyhydroxamic ester is 195° to 196° .¹

The following results were obtained from an analysis of the other fraction:

0.2258 gram gave 0.4299 gram CO_2 and 0.1873 gram H_2O .

	Calc. for $C_7H_{15}O_2N$	Found
C	52.11	52.00
H	9.39	9.29

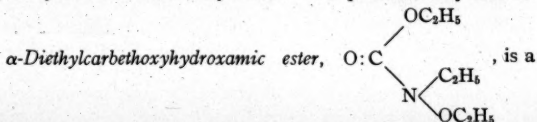
From this it is seen that the impurity which contaminated the neutral portion obtained from the action of ethyl iodide upon the potassium salt of carbethoxyhydroxamic acid was α -ethylcarbethoxyhydroxamic ester.

Action of Ethyl Iodide on α -Ethylcarbethoxyhydroxamic Ester

An alcoholic solution containing the theoretical amount of sodium ethylate was gradually added to a mixture of 14 grams of α -ethylcarbethoxyhydroxamic ester and 16.4 grams of ethyl iodide. The mixture grew warm and sodium iodide soon began to crystallize. After standing at room temperature for two days, the mixture was heated on the water bath at 80° for two hours. Most of the alcohol was then removed by distillation and the residue filtered from the dense precipitate of sodium iodide. The solution was then diluted with water, and extracted repeatedly with ether. The ether solution was shaken several times with dilute alkali to remove unchanged α -ethylcarbethoxyhydroxamic ester, dried with anhydrous sodium sulphate and fractionated. Twelve and one-half

¹ Jones: *THIS JOURNAL*, **30**, 41ff.

grams of the diethyl ester, boiling at 72° – 74° under 12 mm. pressure, were obtained. The yield was 76 per cent. of the theoretical. The oil prepared in this way was identical in every respect with that obtained as the by-product in ethylating hydroxyurethan with ethyl iodide and potassium hydroxide.



colorless oil, with a disagreeable odor suggesting an isocyanide. It is very slightly soluble in water, and is soluble in all proportions in alcohol and ether. It gives no color test with ferric chloride, and does not reduce ammoniacal silver nitrate or Fehling's solution.

Decomposition of α -Diethylcarbethoxyhydroxamic Ester with Potassium Hydroxide

A mixture of 12.5 grams of the diethyl ester and 20 grams of potassium hydroxide dissolved in water was heated together in a sealed tube at 100° for 30 hours. The contents of the tube were then distilled, and the distillate passed into a dilute solution of hydrochloric acid. Since the distillate did not all dissolve in the hydrochloric acid, the solution was extracted with ether. Five grams of the undecomposed ester were recovered from the ether by fractionation. The acidified distillate was concentrated on the water bath and the last portions of water and hydrochloric acid were removed by placing the thick liquid in a vacuum desiccator containing concentrated sulphuric acid and pieces of solid potassium hydroxide. After some time the liquid had solidified to a mass of white crystals, identical with those obtained by Jones.¹ The free base can be obtained by heating a mixture of the dry salt and potassium hydroxide. It was first prepared by Lossen² from the oxalate, and was fully described by him.

¹ Jones: *THIS JOURNAL*, **30**, 418.

² Lossen: *Ann. Chem. (Liebig)*, **252**, 234.

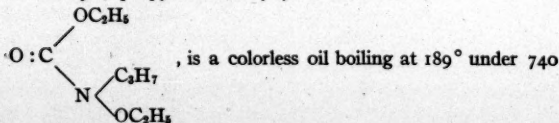
I. α -Ethyl- β -propylhydroxylamine

(a) *Action of Normal Propyl Iodide on α -Ethylcarbethoxyhydroxamic Ester.*—The action of a mixture of normal propyl iodide and sodium ethylate upon α -ethylcarbethoxyhydroxamic ester proceeds very slowly in the cold, but quite rapidly at higher temperatures. Thus, a solution of 35.5 grams of α -ethylcarbethoxyhydroxamic ester, 45.5 grams of normal propyl iodide and the theoretical amount of sodium ethylate in absolute alcohol gave a slight precipitate of sodium iodide after standing at room temperature for four days. The precipitate was filtered from the solution, and this was then heated on the water bath at 80° for half an hour. A dense precipitate formed, which was removed. After the solution had been diluted with water, it was extracted a number of times with ether. The little free iodine which was present was removed with sodium thiosulphate, the ether solution was dried and 33 grams of the α -ethyl- β -propylcarbethoxyhydroxamic ester were obtained by fractionation. The yield was 71 per cent. of the theoretical.

0.4076 gram gave 29 cc. N_2 at 18° and 750 mm. (uncorr.).

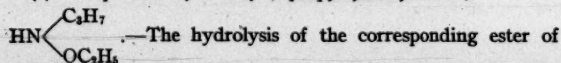
	Calc. for $C_8H_{17}O_3N$	Found
N	8.00	8.11

α -Ethyl- β -propylcarbethoxyhydroxamic ester,



mm. pressure. It has an odor similar to nicotine, and is soluble in water, alcohol and ether. It gives no reaction with ferric chloride, ammoniacal silver nitrate or Fehling's solution.

(b) *Preparation of α -Ethyl- β -propylhydroxylamine,*



—The hydrolysis of the corresponding ester of carbethoxyhydroxamic acid was accomplished most easily as follows: Fifteen grams of the ester, mixed with an aqueous

solution containing 30 grams of potassium hydroxide, were heated in a sealed tube at about 120° for twenty-four hours. The product from the hydrolysis was then treated in the same way as described under α -diethylcarbethoxyhydroxamic ester (see page 451).

α -Ethyl- β -propylhydroxylamine hydrochloride crystallizes in large plates melting at $72.5-73^{\circ}$. This salt is easily soluble in alcohol, benzene, chloroform and toluene. It is not soluble in ether and very slightly soluble in carbon bisulphide. An alcoholic solution of platinic chloride with an alcoholic solution of the hydrochloride gave a solution of the chloroplatinate. By the addition of dry ether to the solution the salt was precipitated as brilliant, deep yellow crystals, which melted at 150.2° .

0.2490 gram gave 0.0794 gram platinum.

	Calc. for $C_{10}H_{21}O_2N_2PtCl_4$	Found
Pt	32.19	31.88

To prepare α -ethyl- β -propylhydroxylamine, the hydrochloride was distilled with an excess of concentrated sodium hydroxide solution, and the vapors passed over pieces of solid sodium hydroxide heated to 95° before they were condensed. It is a clear, colorless liquid boiling at $83.8-84^{\circ}$ and has a sharp ammoniacal odor and a sweet, biting taste. It reduces ammoniacal silver nitrate solution slowly in the cold, and very rapidly when warmed. It does not reduce Fehling's solution in the cold, but does so slowly on being heated. It gives no color reaction with ferric chloride. It is slightly soluble in water, and is soluble in all proportions in alcohol. Its specific gravity is 0.8033 ($25^{\circ}/25^{\circ}$). Its index of refraction at 25° is 1.39426.

II. α -Ethyl- β -isopropylhydroxylamine

(a) Action of Isopropyl Iodide and Sodium Ethylate on α -Ethylcarbethoxyhydroxamic Ester

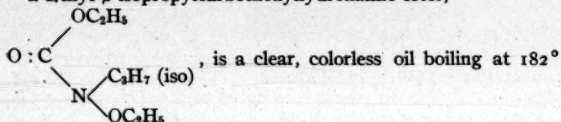
Isopropyl iodide reacts with α -ethylcarbethoxyhydroxamic ester in the presence of sodium ethylate just as its isomer does. Thus, 28 grams of the α -ethyl ester of carbethoxyhydroxamic acid and 36 grams of isopropyl iodide, when treated with the

calculated amount of sodium ethylate dissolved in alcohol, gave a fine, white precipitate of sodium iodide after standing for several days at room temperature. This precipitation was hastened by warming the solution on the water bath. The alcoholic solution was filtered, diluted with water and extracted with ether. The ether solution was then shaken with dilute potassium hydroxide solution, dried and fractionated. Twenty-four grams of α -ethyl- β -isopropylhydroxamic ester were obtained. The yield was 66 per cent. of that required by theory.

0.3015 gram gave 23 cc. N_2 at 24° and 739 mm. pressure (uncorr.).

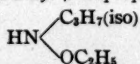
	Calc. for $C_8H_{17}O_3N$	Found
N	8.00	8.27

α -Ethyl- β -isopropylcarbethoxyhydroxamic ester,



under 748 mm. pressure (84° – 87° under 14–15 mm.). It has a strong odor resembling parsnips. Its aqueous solution does not reduce ammoniacal silver nitrate, and gives no coloration with ferric chloride.

(b) Preparation of α -Ethyl- β -isopropylhydroxylamine,



A mixture of 15 grams of α -ethyl- β -isopropylcarbethoxyhydroxamic ester and 25 grams of potassium hydroxide dissolved in water were heated in a sealed tube at 120° – 160° for 36 hours. The aqueous solution of the free base, thus formed, was distilled, and the distillate passed into dilute hydrochloric acid. All of the ester had been hydrolyzed. Another tube, charged in the same way and heated to 110° for forty hours, gave five grams of unhydrolyzed ester on extraction of the acidified distillate with ether. The solution of the hydrochloride was concentrated by evaporation on the

water bath, and then placed in a vacuum desiccator containing concentrated sulphuric acid and potassium hydroxide. The salt had not crystallized from the liquid after one month, so the liquid was placed in a vacuum desiccator over phosphorus pentoxide and kept at room temperature for one week, then at 0° for a week. By this treatment a syrupy liquid, intermixed with a few tiny crystals (probably ammonium chloride), was obtained. A mixture of 3 grams of this syrupy hydrochloride with 6 grams of powdered potassium hydroxide was dry distilled and gave 1.90 grams of the free base.

α -Ethyl- β -isopropylhydroxylamine is a clear, colorless liquid boiling at 78° . It has an odor very much like that of ethylamine. Its specific gravity ($25^{\circ}/25^{\circ}$) is 0.8132. The base is soluble in a large amount of water and this solution does not reduce ammoniacal silver nitrate in the cold, but does so rapidly when warmed. It does not reduce Fehling's solution when hot or cold.

An alcoholic solution of platinic chloride precipitated the chloroplatinate from a hot alcoholic solution of the hydrochloride as small lemon-yellow crystals. These decomposed without melting when heated.

0.2060 gram gave 0.0660 gram Pt.

	Calc. for $C_{10}H_{19}O_2N_3PtCl_6$	Found
Pt	32.19	32.04

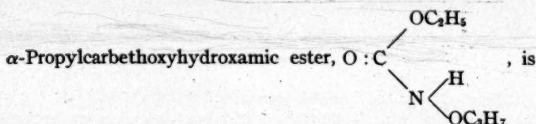
III. α -Propylhydroxylamine, $H_2NOC_3H_7$

(a) *Action of Normal Propyl Iodide on the Potassium Salt of Hydroxyurethan.*—When an alcoholic solution containing 33.6 grams of potassium hydroxide was slowly added, with constant shaking, to a mixture of 64 grams of normal propyl bromide, 13.6 grams of normal propyl iodide and 63 grams of hydroxyurethan, the mixture became turbid and the temperature rose slightly. The flask was, therefore, cooled to prevent, as far as possible, the hydrolysis of the mono ester by the potassium hydroxide. After standing for a week at room temperature, the mixture was heated for one-half hour at 80° . The salt which had precipitated was removed by filtration, most of the alcohol was distilled off, the remaining solution

was diluted with water and extracted repeatedly with ether. The ether solution was then shaken with the calculated amount of a dilute solution of potassium hydroxide. The ether solution which was left contained the dipropylcarbethoxyhydroxamic ester (see below), and the water solution contained the monopropylcarbethoxyhydroxamic ester in the form of the potassium salt. To obtain the free ester, the alkaline solution was acidified with 10 per cent sulphuric acid, and extracted with ether. The ether solution was colored by a little free iodine, which was removed with sodium thiosulphate solution. The ether solution was dried and then fractionated under diminished pressure, since the ester decomposes somewhat when distilled under atmospheric pressure. The yield was 32 grams, only 36.3 per cent. of the theoretical yield.

0.3119 gram gave 28.3 cc. N_2 at $23^\circ.5$ and 733.8 mm.

	Calc. for $C_9H_{19}O_3N$	Found
N	9.55	9.84



a colorless oil boiling at 109° – 111° under 15 mm. pressure. At atmospheric pressure it boils between 200° and 210° with slight decomposition. It is not appreciably soluble in water, but is soluble in all proportions in alcohol and in ether. It has a faint, pleasant odor.

The ether solution of the dipropylcarbethoxyhydroxamic ester (see above) was dried with anhydrous sodium sulphate and fractionated. Nine and one-half grams (8.5 per cent. of the theoretical) of dipropylcarbethoxyhydroxamic ester were obtained. It is a clear, colorless oil, insoluble in water, boiling at $107^\circ.5$ – 108° under 20 mm. pressure. It has an odor resembling roasted chestnuts.

0.3192 gram gave 23 cc. N_2 at 22° and 740 mm. pressure.

	Calc. for $C_9H_{19}O_3N$	Found
N	7.40	7.80

(b) Preparation of α -Propylhydroxylamine, $\text{HN} \begin{matrix} \text{H} \\ \diagup \\ \text{OC}_3\text{H}_7 \end{matrix}$

Ten grams of α -propylcarbethoxyhydroxamic ester and 20 grams of potassium hydroxide dissolved in water formed a homogeneous mixture. This mixture was heated in a sealed tube at 100° for 12 hours. The resulting products from the hydrolysis were distilled and the distillate collected in dilute hydrochloric acid. This was concentrated by evaporation on the water bath, and then placed in a vacuum desiccator containing concentrated sulphuric acid and solid potassium hydroxide. α -Propylhydroxylamine hydrochloride crystallized from the solution in large, thin, transparent white plates, which melted at 140° – 141° . The salt is very soluble in water and in alcohol, but insoluble in ether. It is not deliquescent. An alcoholic solution of platinic chloride precipitated the chloroplatinate as light yellow crystals from an alcoholic solution of the hydrochloride.

0.1103 gram gave 0.0408 gram Pt.

Calc. for $(\text{C}_3\text{H}_7\text{ON})_2\text{PtCl}_6$		Found
Pt	35.48	36.89

When a mixture of 2.67 grams of α -propylhydroxylamine hydrochloride and 6 grams of finely powdered potassium hydroxide was subjected to dry distillation, 1.35 grams of a clear, colorless liquid, having a sweetish, ammoniacal odor, were obtained. The yield was 75 per cent. of the theoretical. α -Propylhydroxylamine boils at 86.6 – 87° . Its specific gravity ($25^\circ/25^\circ$) is 0.8687. Its aqueous solution rapidly reduces ammoniacal silver nitrate and Fehling's solution in the cold.

IV. α -Propyl- β -ethylhydroxylamine, $\text{HN} \begin{matrix} \text{C}_2\text{H}_5 \\ \diagup \\ \text{OC}_3\text{H}_7 \end{matrix}$

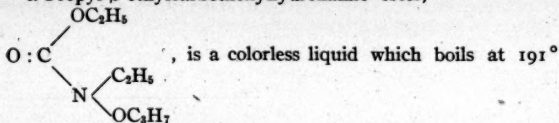
(a) Action of Ethyl Iodide on α -Propylcarbethoxyhydroxamic Ester.—Five grams of sodium dissolved in alcohol were slowly added to an alcoholic solution containing 32 grams of α -propylcarbethoxyhydroxamic ester and 35 grams of ethyl iodide. The mixture was allowed to stand at room temperature for a week, and was then heated to 70° for four hours

to complete the reaction. Most of the alcohol was then distilled off, the solution was diluted with water and extracted with ether. The ether extract was shaken with dilute potassium hydroxide solution to remove free iodine and any unchanged monopropyl ester present, then dried with sodium sulphate. After a few hours, the solution became dark brown, due to free iodine. Repeated shaking with sodium thiosulphate solution was necessary to remove all of the color. The solution was again dried and fractionated under 750 mm. pressure. Thirty grams of α -propyl- β -ethylcarbethoxyhydroxamic ester were obtained. The yield was 79 per cent. of the theoretical.

0.3512 gram gave 27 cc. N_2 at 27° and 750.4 mm. pressure.

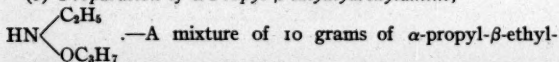
	Calc. for $C_8H_{17}O_3N$	Found
N	8.00	8.33

α -Propyl- β -ethylcarbethoxyhydroxamic ester,



under 750 mm. pressure without decomposition ($92^\circ.5$ under 20 mm.). It has an odor similar to α, β -diethylcarbethoxyhydroxamic ester. It is not soluble in water, but is very soluble in alcohol and in ether.

(b) *Preparation of α -Propyl- β -ethylhydroxylamine,*



carbethoxyhydroxamic ester and 20 grams of potassium hydroxide dissolved in water was heated in a sealed tube at 130° for 24 hours. The contents of the tube were then treated in the customary manner, and the hydrochloric acid solution extracted with ether. One-half gram of unhydrolyzed ester was recovered from the ether extract. The acid solution was concentrated on the water bath. During this operation considerable α -propyl- β -ethylhydroxylamine hydrochloride was lost by volatilization. Only 1.7 grams of α -propyl- β -ethyl-

hydroxylamine hydrochloride was obtained. This was purified by precipitation with ether from an alcoholic solution. It forms large, lustrous crystals, resembling benzoic acid in appearance, which melt without decomposition at $96^{\circ}.2$. It is moderately soluble in cold chloroform and readily soluble in boiling chloroform, from which it crystallizes on cooling. It is very deliquescent. Its aqueous solution does not reduce ammoniacal silver nitrate or Fehling's solution, either cold or hot. An alcoholic solution of platinic chloride precipitated the chloroplatinate from an alcoholic solution of the hydrochloride as small, light yellow crystals, which decomposed when melted.

When 1.14 grams of the hydrochloride were mixed with 4 grams of finely powdered potassium hydroxide and distilled, 0.31 gram of a clear, colorless liquid, having an odor similar to its isomer, was obtained. α -Propyl- β -ethylhydroxylamine is moderately soluble in water, and this solution reduces ammoniacal silver nitrate slowly in the cold and rapidly on warming. It does not reduce Fehling's solution either hot or cold. The free base is very volatile.

V. α -Dipropylhydroxylamine

(a) *Hydrolysis of α,β -Dipropylcarbethoxyhydroxamic Ester.*—Fifteen grams of dipropylcarbethoxyhydroxamic ester and 20 grams of potassium hydroxide were heated together in a sealed tube at 130° for 40 hours. The contents of the tube were then treated in the usual way, and the hydrochloride of α -dipropylhydroxylamine obtained as white crystals, mixed with a little ammonium chloride. The salt was easily purified by dissolving the impure product in absolute alcohol, filtering from the ammonium chloride, and then adding absolute ether. This precipitated the salt as small, lustrous crystals, which melted at $146^{\circ}.6$. These crystals were extremely soluble in water but were not at all deliquescent. When an alcoholic solution of platinic chloride was added to an alcoholic solution of the hydrochloride, deep yellow crystals of the chloroplatinate were precipitated.

0.1634 gram gave 0.0498 gram Pt.

	Calc. for $C_3H_7NO_2NaPtCl_4$	Found
Pt	30.29	30.47

By distillation of 3 grams of the hydrochloride with finely powdered potassium hydroxide, 1.76 grams of α,β -propylhydroxylamine were obtained. The yield is 77 per cent. of the theoretical. It is a clear, colorless liquid boiling at 85° – 86° . Its specific gravity ($25^\circ/25^\circ$) is 0.8141. It is somewhat soluble in water, and this solution instantly reduces ammoniacal silver nitrate solution in the cold, but has no effect upon Fehling's solution even when boiled with it.

VI. α -Isopropylhydroxylamine

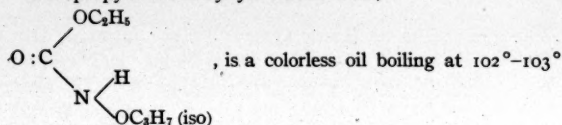
(a) *Action of Isopropyl Halides on the Potassium Salt of Carbethoxyhydroxamic Acid.*—Isopropyl halides react with difficulty with the sodium and potassium salts of carbethoxyhydroxamic acid. When the usual method for carrying out the reaction between isopropyl halides and carbethoxyhydroxamic acid in the presence of potassium hydroxide was tried, it was found impossible to increase the yield of the monoisopropylcarbethoxyhydroxamic ester much above 20 per cent. Usually the yield was lower than this. The following data represent an average experiment: Thirty-one grams of isopropyl bromide and 40 grams of isopropyl iodide were added to 51 grams of carbethoxyhydroxamic acid dissolved in 25 cc. of absolute alcohol. The mixture was cooled and then an alcoholic solution of potassium hydroxide, containing a little less than the theoretical amount, was slowly added, with constant shaking of the mixture. The mixture was kept cool for a day, then allowed to stand at room temperature for three days, and finally heated to 90° for fifteen minutes to complete the reaction. The alcoholic solution was then treated in the usual manner, and 13 grams of α -isopropylcarbethoxyhydroxamic ester were obtained. The yield was 18.3 per cent. of the theoretical.

The next method which was tried was to isolate the sodium salt of hydroxyurethan and suspend it in alcohol. The theoretical quantity of isopropyl halide was added, and the mixture was then boiled under a reflux condenser for a day. The re-

action mixture was then worked up, but a smaller yield of the ester was obtained than before.

The following method gave the best results: A mixture of 25 grams of hydroxyurethan, 29.3 grams of isopropyl bromide and about 15 grams of alcohol was boiled under a reflux condenser. An alcoholic solution of 13.3 grams of potassium hydroxide was added very slowly to the boiling solution. A heavy precipitate separated out. The resulting solution was then treated in the usual manner. Six grams of unchanged isopropyl bromide were recovered. Ten grams of α -mono-isopropylcarbethoxyhydroxamic ester were obtained, representing a yield of 36 per cent.

α -Isopropylcarbethoxyhydroxamic ester,



under 12 mm. pressure. It is slightly soluble in water, and does not reduce ammoniacal silver nitrate solution. It colored ferric chloride purple, due to a trace of hydroxyurethan which was carried over with it. Unlike the other alkyl derivatives of carbethoxyhydroxamic acid, it has practically no odor.

0.3098 gram gave 0.5482 gram CO_2 and 0.2158 gram H_2O .

	Calc. for $\text{C}_6\text{H}_{13}\text{O}_3\text{N}$	Found
C	48.91	48.30
H	8.91	9.02

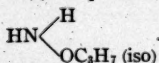
The ether solution containing the α,β -diisopropylcarbethoxyhydroxamic ester, which was left after the mixture of the mono- and diisopropyl esters had been extracted with potassium hydroxide solution, was dried and fractionated. An oil boiling at 101° – 101.5° under 15 mm. pressure was obtained. Eight and a half per cent. of the carbethoxyhydroxamic acid had been converted into the dialkyl derivative.

0.2760 gram gave 0.5754 gram CO_2 and 0.2524 gram H_2O .

	Calc. for $\text{C}_8\text{H}_{19}\text{O}_3\text{N}$	Found
C	57.09	56.85
H	10.13	11.76

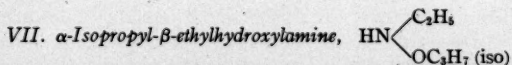
α,β -Diisopropylcarbethoxyhydroxamic ester is slightly soluble in water. This solution gives no reaction with ferric chloride, ammoniacal silver nitrate or Fehling's solution. It has a pleasant odor, very much like that of phenylacetic ester.

(b) *Preparation of α -Isopropylhydroxylamine,*



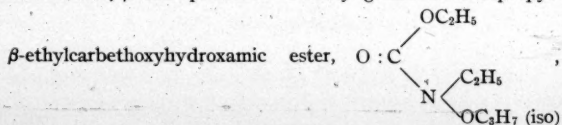
—The hydrolysis of the α -isopropylcarbethoxyhydroxamic ester was accomplished in the customary manner. Five and one-half grams of the ester, mixed with a solution containing 10 grams of potassium hydroxide, were heated at 100° for twenty-four hours. The free base was distilled from the aqueous solution and collected in dilute hydrochloric acid. This solution was concentrated and placed in a vacuum desiccator with potassium hydroxide and sulphuric acid. After two weeks α -isopropylhydroxylamine hydrochloride had crystallized out as white plates, melting at $84^\circ.8$, which were deliquescent. (Compare the isomeric *n*-propylhydroxylamine hydrochloride.) It is soluble in water and alcohol, but not soluble in ether. Its aqueous solution rapidly reduces silver nitrate and Fehling's solution in the cold.

Free α -isopropylhydroxylamine was obtained by distilling a mixture of 2 grams of the hydrochloride and 4 grams of dry potassium hydroxide. It is a colorless liquid boiling at $72^\circ.2$ (uncorr.). It has a disagreeable, pungent odor. Its specific gravity ($25^\circ/25^\circ$) is 0.8459. Its aqueous solution reduces ammoniacal silver nitrate solution and Fehling's solution.



(a) *Action of Ethyl Iodide on α -Isopropylcarbethoxyhydroxamic Ester.*—A solution of 4.22 grams of sodium in absolute alcohol was slowly added to an alcoholic solution containing 27 grams of α -isopropylcarbethoxyhydroxamic ester and 28.6 grams of ethyl iodide. No noticeable change occurred. The mixture was allowed to stand for two weeks at room temperature, and was then heated to 70° for several hours. The small

amount of fine precipitate was removed, most of the alcohol was distilled off, and after diluting the solution with water it was extracted with ether. The ether extract was shaken with dilute potassium hydroxide solution, and then shaken repeatedly with sodium thiosulphate solution to remove the free iodine which was present. It was then dried and fractionated under 748 mm. pressure. Twenty grams of α -isopropyl-



boiling at 181° – 182° were obtained. The yield was 62.5 per cent. of the theoretical.

0.3499 gram gave 26 cc. N at 20° and 743.5 mm. pressure.

	Calc. for $\text{C}_8\text{H}_{17}\text{O}_3\text{N}$	Found
N	8.00	8.29

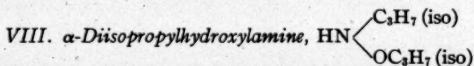
α -Isopropyl- β -ethylcarbethoxyhydroxamic ester is soluble in water, alcohol and ether. It gives no reaction with either ammoniacal silver nitrate, Fehling's solution or ferric chloride. It has a biting odor resembling phosgene.

(b) *Preparation of α -Isopropyl- β -ethylhydroxylamine.*—Ten grams of the ester were treated in the usual manner with 20 grams of potassium hydroxide dissolved in water. The hydrochloride of α -isopropyl- β -ethylhydroxylamine, which was formed, remained as an oil upon evaporating the aqueous solution and drying in a desiccator over sulphuric acid. The aqueous solution of the salt reduced ammoniacal silver nitrate in the cold. Platinic chloride precipitated the chloroplatinate as a light yellow crystalline powder from an alcoholic solution of the hydrochloride.

0.1328 gram gave 0.0436 gram Pt.

	Calc. for $\text{C}_{10}\text{H}_{21}\text{O}_2\text{N}_2\text{PtCl}_4$	Found
Pt	32.19	32.83

When the hydrochloride is distilled with potassium hydroxide it gives α -isopropyl- β -ethylhydroxylamine. This is a colorless liquid boiling at 82° . It has an ammoniacal odor, and is not very soluble in water. Its aqueous solution reduces ammoniacal silver nitrate in the cold and Fehling's solution when heated. Its specific gravity ($25^\circ/25^\circ$) is 0.8730.



A mixture of 13 grams of α,β -diisopropylcarbethoxyhydroxamic ester and 25 grams of potassium hydroxide dissolved in water were heated at 120° in a sealed tube for 36 hours. The contents of the tube were then distilled, and treated as usual. The hydrochloride of diisopropylhydroxylamine slowly crystallized out, mixed with ammonium chloride. The salt was recrystallized from alcohol. It formed flat plates, which melted at $74^\circ.8$.

Ten grams of powdered potassium hydroxide were poured over 5 grams of the hydrochloride contained in a distilling flask, and the mixture was warmed. Three and one-tenth grams of the free base were obtained. The yield was 82 per cent. of the theoretical. α -Diisopropylhydroxylamine is a colorless liquid boiling at $76.6\text{--}77^\circ$. It has an ammoniacal odor mixed with that of an isocyanide. It is readily soluble in water, and rapidly reduces ammoniacal silver nitrate in the cold. It does not reduce Fehling's solution. Its specific gravity ($25^\circ/25^\circ$) is 0.8525.

The following table summarizes the properties of these compounds:

	Esters of hydroxyurethan	Free base		Hydrochloride.
		B. p.	Sp. gr.	M. p.
α -Ethyl	195°-196° 95°-97° at 17 mm.	68° (Lossen)	0.8827 (Lossen)	128° E. (Lossen)
α -Propyl	200°-210° E. 109°-111° at 15 mm.	86°-6-87°	0.8687	140°-141°
α -Isopropyl	102°-103° at 12 mm.	72°-2	0.8459	84°-8
α,β -Diethyl	72°-74° at 12 mm.	83° (Lossen)	0.829 at 0° (Lossen)	123°-124° (Jones)
α,β -Dipropyl	107°-5-108° at 20 mm.	85°-86°	0.8141	146°-6
α,β -Diisopropyl	101°-101°-5 at 15 mm.	76°-6-77°	0.8525	74°-8
α -Ethyl- β -propyl	189°	83°-8-84°	0.8033	72°-5-73
α -Ethyl- β -isopropyl	182° 84°-87° at 15 mm.	78°	0.8132	oil
α -Propyl- β -ethyl	92°-5 at 20 mm. 191°			96°-2
α -Isopropyl- β -ethyl	181°-182°	82°	0.8730	oil

SUMMARY

1. In the present paper methods of preparing the ethyl, propyl and isopropyl esters and mixed ethyl propyl and ethyl isopropyl esters of carbethoxyhydroxamic acid are described and the compounds studied. These esters are all high boiling oils with a characteristic odor. None of them reduce ammoniacal silver nitrate or Fehling's solution.

2. α -Propylhydroxylamine, α -isopropylhydroxylamine, and the different possible α -dialkylhydroxylamines containing ethyl, propyl and isopropyl groups, also their hydrochlorides and chloroplatinates, have been made and studied.

3. It has been shown that the esters of carbethoxyhydroxamic acid suffer hydrolysis with potassium hydroxide, the more easily the higher the molecular weight of the substituting group.¹

4. The specific gravity of the dialkyl derivatives of hydroxylamine is less than the specific gravity of the monoalkyl derivatives of hydroxylamine, and all are specifically lighter than water. All boil between 70° and 90°.

5. The monoalkylhydroxylamines and the dialkylhydroxylamines containing two like groups are soluble in water, while the mixed dialkylhydroxylamines require a large amount of water for solution.

6. The aqueous solutions of the α -monoalkylhydroxylamines are energetic reducing agents. A second alkyl group in the molecule diminishes the reducing action.

In conclusion, I desire to express my sincere thanks to Dr. Lauder W. Jones, under whose direction the present work was carried out, for his kindly interest and many helpful suggestions and criticisms.

UNIVERSITY OF CINCINNATI
June 1, 1913

OBITUARY

JULIUS LEWKOWITSCH

Julius Lewkowitsch, who died at Chamonix, Switzerland, September 15th, after a brief illness, was born at Ostrowo,

¹ Experiments made in this laboratory by Miss Leonora Neuffer on the secondary butyl derivatives confirm this statement.

Prussian Silesia, in 1857. Receiving his preparatory education in his native place, he went to Breslau, where he worked under Victor von Richter and won his Ph.D. degree in 1879 and that of M.A. in 1881. He then accepted a position at the Friedrichs Real Gymnasium, Berlin, under Landolt, and later became assistant to Victor Meyer at Heidelberg. During these years, he published a number of papers dealing with the action of nitric acid on fats and with stereochemical subjects, mandelic acid, optically active glyceric acids and leucine. He now turned to industrial chemistry and for a time was connected with tar and petroleum works. Going to England, he entered the employ of the Whitehall Soap Works at Leeds, and the remainder of his life was devoted chiefly to the technology of vegetable and animal oils and fats, a subject in which he became one of the world's greatest authorities. It was at Leeds that he, for the first time, succeeded in obtaining pure glycerol from soapmakers' lyes. Many of the processes now used in the utilization and analysis of these substances were devised or improved by him. In 1895, he started practice at Manchester as a Consulting Chemist and Technologist in Oils and Fats. Three years later he removed to London, and for many years acted as examiner for the City and Guilds of London Institute.

Lewkowitsch was a prolific writer and his works have come to be regarded as standards on their subjects. In 1895 he published his book on Oils and Fats, known in later editions as "The Chemical Technology of Oils, Fats and Waxes," the first volume of the fifth edition of which came from the press a few days before his death. French and German translations of this masterly work have also appeared. He also contributed the article on Oils and Fats to the Encyclopedia Britannica and the articles on these subjects and on Margarin to Thorpe's Dictionary of Chemistry and covered these fields in Meyer's "Jahrbuch der Chemie" and Lunge's "Chemisch-technische Untersuchungsmethoden." Among his other books may be mentioned his "Laboratory Companion to Fats and Oils Industries," which has also been translated into German. His total contributions to scientific literature number about 140.

He early became connected with the "Journal of the Society of Chemical Industry," first as Abstractor, then as a member of the Publication Committee, and served on the Council and as Vice-President of the Society. He was Chairman of the London Section at the time of the meeting of the International Congress of Applied Chemistry at London, and his remarkable linguistic versatility is shown by the fact that he

addressed that gathering in English, German, French and Italian. In 1911, he was made Foreign Secretary of the Society, a position he held at the time of his death. He also served on the Councils of the Institute of Chemistry, of the London Chemical Society and of the Society of Public Analysts. In 1909 he was awarded the Lavoisier medal of the French Chemical Society.

REVIEWS

A TEXTBOOK OF CHEMISTRY. By WILLIAM A. NOYES, Director of the Chemical Laboratory of the University of Illinois. New York: Henry Holt and Company. 1913. pp. xv + 602.

The author tells us that: "This book is the result of twenty-five years of experience in teaching chemistry to classes of students, some of whom were beginning the subject while others have had an elementary course in the High School. It is intended to make the presentation sufficiently complete and clear so that college students who have had an elementary course in physics may use the book successfully, without any previous study of chemistry. At the same time it is believed that the book is of such a character that the college students who use it after taking a course in the High School will not feel that they are wasting their time."

The book is clearly written and is, no doubt, accurate. What especially distinguishes it from most other books prepared for the same general purpose is the amount of space devoted to the newer theories. Descriptive chemistry is, however, not treated as if of minor importance.

Opinions differ as to how profitable it is for college students beginning the subject to attempt to acquaint themselves with all the latest conceptions, some of which it is impossible for them even faintly to comprehend. Assuming that it is well for them to make the effort, this book can be highly recommended as a guide.

The author is unusually cautious and this has led him to use such expressions as "for some reason," p. 8; "it is well, however, to recognize how imperfect and fragmentary our knowledge is and that there are hundreds of questions like these for which we have no answer," p. 28; "This is another of those questions, like the cause of heat generated when elements combine, which waits for an answer," p. 29; "for other reasons which we do not fully understand," p. 50; "Other factors are involved, and some of these are, at present, but little understood," p. 52; "No satisfactory reason for such differences has been discovered," p. 79; "but we can form

only a very vague idea of the mechanism of the action," p. 105; "The reason for this catalytic effect of the water is not understood," p. 105; "but it is also connected with the change in volume which occurs in the reaction and with other factors which are less clearly understood," p. 110; etc.

Such expressions show, to be sure, that the state of mind of the author is thoroughly scientific, but it is fair to ask whether they are wise pedagogically? A certain amount of dogmatism is necessary in teaching beginners, otherwise there is some danger that they will take all statements with a grain of salt. The writer recalls an experience of his early years, when he was beginning his work as a teacher. He was at that time, and is still, very much impressed by the immensity of the unknown and in lecturing he was apt to use the expression "but, in fact, we know very little about this subject." One day, on pressing a student who had struck bottom in recitation, he was amused and surprised and made wiser by the answer: "We know very little about this subject, professor." The professor was extremely cautious after that in using that expression. This is not intended as a suggestion that Professor Noyes's book is seriously marred by the tendency illustrated. It isn't. In the opinion of the writer the book is an excellent one and deserves a conscientious trial.

I. R.

OUTLINES OF THEORETICAL CHEMISTRY. By FREDERICK H. GETMAN, Ph.D. (Johns Hopkins), Associate Professor of Chemistry in Bryn Mawr College. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1913. pp. 467. Price, \$3.50.

The author of this admirable little book states in his preface that "the present book is designed to meet the requirements of classes beginning the study of theoretical or physical chemistry. A working knowledge of elementary chemistry and physics has been presupposed in the presentation of the subject, the introductory chapter being the only portion of the book in which space is devoted to a review of principles with which the student is assumed to be already fairly familiar. With the exception of a few paragraphs in which the application of the calculus is unavoidable, no use is made of the higher mathematics, so that the book should be intelligible to the student of very moderate mathematical attainments."

The "contents" and order of arrangement of the material are just about what one would expect in a book designed for elementary students in "general chemistry."

The most striking features of the book are: it is written in clear, and, usually, choice English, from which all of the life has not been taken by repeated revision. The illustrations

are admirably drawn, and the publishers have done a good piece of "book-making." It is to be hoped that this book will find a demand that is commensurate with its pronounced merits.

H. C. J.

ELEMENTARY CHEMISTRY, with Special Reference to the Chemistry of Medicinal Substances. By H. M. GORDIN, Professor of Chemistry in the Schools of Pharmacy and Dentistry of the Northwestern University. Vol. I, Inorganic Chemistry. Chicago: Medico-Dental Publishing Co. pp. 482. Price, \$3.00.

The author's purpose in writing this book may best be understood by the following quotation from the preface: "The book is intended primarily for those studying for, or engaged in, the professions of pharmacy, medicine and dentistry. In addition to the material usually treated in elementary text-books on inorganic chemistry, it contains most of the inorganic chemicals, both official and non-official, employed as medical agents." The book is not intended for a laboratory manual, but as an explanation of the chemical principles "underlying the preparation, identification, and assay of substances used in the healing professions." Several chapters on energy, matter, physical and chemical changes, gas laws, molecular and atomic hypotheses, the determination of chemical formulas, and chemical equations serve as an introduction. Theoretical chapters on valence, solution, electrolysis, ionic theory, etc., are then interspersed with the usual description of the elements and their compounds. However, one notes the lack of the application of these principles to specific examples. The treatment of the theoretical side is simpler than in most similar text-books, but in some cases accuracy is sacrificed to simplicity and reminds one of kindergarten methods. Thus on page 5 we read of substances being divided into "ponderable substances" and "imponderable substances," and a few lines below, "heat and electricity are examples of imponderable substances." On page 48, "ready-made hydrogen," on page 54, "ready-made oxygen," on page 113, "that substance which is made to disappear in the other is said to be dissolved," and on page 178, "to fence off the elements into closed groups," are rather unusual.

A medical atmosphere is given the book by brief descriptions of various pharmacopoeial tests, but these are too incomplete to be of any use in the actual performance of the test. The various methods of balancing equations receive a very full discussion, and a set of questions and problems concludes each chapter.

E. K. MARSHALL, JR.

COURS ÉLÉMENTAIRE DE CHIMIE ET DE MINÉRALOGIE. Par DR. C.-I. ISTRATI, Professeur de Chimie organique à l'Université de Bucarest, et DR. G.-G. LONGINESCU, Professeur de Chimie inorganique à l'Université de Bucarest. Avec une Préface de CHARLES FRIEDEL, Membre de l'Institut. Deuxième édition française, publiée d'après la quatrième édition roumaine par A. ADAMS, Professeur agrégé au Lycée de Charleville. Paris: Gauthiers-Villars: 1913. pp. xii + 402. Price: paper, Fr. 13.00; cloth, Fr. 14.50.

Owing to the space devoted to mineralogy and the attempt to cover the fields of both organic and inorganic chemistry, the explanations and statements are in many cases brief and unsatisfactory.

J. E. G.

LABORATORY EXPERIMENTS IN GENERAL CHEMISTRY. By H. B. NORTH, Ph.G., D.Sc., Associate Professor of Chemistry in Rutgers College. 36 illustrations. New York: D. Van Nostrand Co. 1913. pp. v + 205. Price, \$1.00.

The experiments in this book, amounting to 500, have been so selected that from them a sufficient number can be chosen to accompany the use of any text-book and to suit any class of students. The experiments are well selected, well presented and especially emphasize the quantitative side of the reactions. The book is well printed and makes an excellent impression. Those who are conducting courses in general chemistry should examine the book carefully as it could be used to great advantage in place of some of the manuals which are now being employed.

J. E. G.

QUANTITATIVE ANALYSIS BY ELECTROLYSIS. By ALEXANDER CLASSEN, with the Coöperation of H. CLOEREN. Translated from the Thoroughly Revised Fifth German Edition by WILLIAM T. HALL, Assistant Professor, Massachusetts Institute of Technology. New York: John Wiley & Sons, Inc. London: Chapman & Hall, Ltd. 1913. pp. xiv + 308. Price, \$2.50.

The German original of this work is so well and favorably known that it is only necessary to note that the translation has been prepared by Prof. Hall to insure for it a welcome by all English-speaking chemists who ever have occasion to make electrolytical analyses. Prof. Hall has made but few changes. He has adopted the system of notation recommended in the report by the Committee on the Notation of Physico-chemical Quantities which was submitted to the Council of the American Chemical Society in March, 1912. The typography, illustrations, paper and binding are up to the Wiley standard.

C. A. R.

QUANTITATIVE ANALYSIS IN PRACTICE. An Introductory Course Designed for Colleges and Universities. By JOHN WADDELL, B.A. (Dalhousie University), B.Sc. (London), Ph.D. (Heidelberg), D.Sc. (Edinburgh), Assistant Professor of Chemistry, School of Mining (Queen's University), Kingston, Canada. London: J. & A. Churchill. Philadelphia: P. Blakiston's Son & Co. 1913. pp. vi + 162. Price, \$1.25.

In the opinion of the reviewer the strong feature of this book is the completeness and discrimination with which the precautions necessary for exact results are described. In almost every case the student is told how to work in a most approved fashion. One serious omission is that the advisability of washing precipitates with a solution of precipitant is not always mentioned, although this procedure is recommended in some instances. The discussions of the various difficulties and remedies are on the whole satisfactory, but it is a pity that the Electrolytic Dissociation Hypothesis is not applied in the main body of the text instead of being confined to an appendix. There the common ion effect on the solubility of precipitates is discussed and applied to the question of completeness of a precipitation, but not to the washing of precipitates. One might criticize also the omissions of any discussion of significant figures, of the determination of nitrogen in the chapter headed "Water Analysis" and of any directions for making sure that the solution is homogeneous before the final setting in adjusting the volume of a standard solution. For pedagogical purposes a table of atomic weights would be more useful than a table of factors. The style occasionally becomes colloquial but it is clear. For instance, the meaning of the direction, "squirt off the cover glass into the casserole," is unmistakable, even if the expression lacks finish. G. P. B.

QUALITATIVE ANALYSE VOM STANDPUNKTE DER IONENLEHRE. Von DR. WILHELM BÖTTGER, A. O. Professor und Oberassistent am phys.-chem. Institut der Universität Leipzig. Dritte Auflage. Mit 26 Figuren im Text, einer Spektraltafel und besonderen Tabellen zum Gebrauche im Laboratorium. Leipzig: Verlag von Wilhelm Engelmann. 1913. S. xvii + 565. Preis, geh., M. 11.20; geb., M. 12.50.

The appearance of the third edition of this very comprehensive treatise on the theory and practice of qualitative analysis is a sufficient indication of its popularity. It is unquestionably the very best modern book on the subject. The third edition, in matter and arrangement, is very similar to the second. Microchemical reactions constitute a new feature. Somewhat more attention is given to colloids and the chapter on oxidation and reduction has been largely rewritten.

B. F. L.

QUALITATIVE CHEMICAL ANALYSIS. A Laboratory Guide. By WILFRED WELDAY SCOTT, A.M., First Assistant Chemist, General Chemical Company, Laurel Hill, N. Y. City, Instructor of Quantitative Analysis, Pratt Institute, Brooklyn. Illustrated. Second Edition, Thoroughly Revised. New York: D. Van Nostrand Co. 1913. pp. xi + 167. Price, \$1.50.

The first edition of this book was very favorably reviewed by Prof. Renouf in *THIS JOURNAL*.¹ The present edition "has been thoroughly revised, portions rewritten and useful material added." The principal changes noted are the addition of a table of atomic weights, rapid qualitative tests for lead, antimony, tin and copper in alloys, Hinds's method for the precipitation of the hydrogen sulphide group and the separation of its divisions, Allen and Palmer's modified Gutzzeit method for arsenic, and tests for salicylic acid.

C. A. R.

PRACTICAL CHEMISTRY. Qualitative Exercises and Analytical Tables for Students. By the late J. CAMPBELL BROWN, D.Sc., LL.D., Professor of Chemistry in the University of Liverpool. Sixth Edition, edited by GUY D. BENGOUGH, M.A., D.Sc. London: J. & A. Churchill. 1913. pp. 78. Price, 2s. 6d.

The author has adopted the usual methods of separation and treatment of the subject, but he has added a section on the reactions of the rare metals and has omitted reference to the relations of the modern theories of ionic reactions and of the mass law to qualitative analysis.

J. E. G.

DIE APPARATFÄRBEREI DER BAUMWOLLE UND WOLLE unter Berücksichtigung der Wasserreinigung und der Apparatbleiche der Baumwolle. Von E. J. HEUSER. Mit 191 in den Text gedruckten Figuren. Berlin: Verlag von Julius Springer. 1913. pp. v + 301. Price, M. 8.00.

To one accustomed to the English books on dyeing and bleaching apparatus, this book immediately impresses the reader as being something different. Although containing nearly two hundred illustrations, there are none of the stereotyped ones which have appeared with great regularity in nearly every English book on the subject since the time of Hummel. It is, strictly speaking, a German book, for only one English and no American machines are described.

The book is divided into four parts: Part I (44 pages) is devoted to a description of apparatus for the purification of water for textile purposes. The recently introduced Permutit system of purification, which has attracted so much attention, is taken up with considerable detail. Part II is divided into two sections, the first (40 pages) being devoted to machinery for bleaching cotton material. All manufacturers

¹ Vol. 46, p. 314.

of cotton cloth woven from dyed yarn realize the great advantages to be derived from a successful cop-dyeing process. Much time and money have been spent in experimenting along this line, particularly in Germany, and those interested in this type of apparatus will find the descriptions and discussions in this book very complete. Part III (65 pages) is devoted to the dyeing of wool in the loose state, and at the different stages of its manufacture into cloth. The modern tendency in dyeing wool as well as cotton is towards the circulatory process, *i. e.*, a process in which the material is kept stationary while the dyeing liquor is circulated through it. Worsted top dyeing by this general method has been in use for a number of years, and the tendency is more and more toward the dyeing of loose wool and even yarn by this method. The Germans have progressed quite rapidly in this direction, and a number of machines of this type are fully described. Part IV (23 pages) is devoted to drying and hydro-extracting apparatus. The book closes with an excellent index which gives, in a tabulated form, the manufacturer's name, use of, number of the illustration, and pages of description for each machine mentioned in the text.

This book will prove a valuable addition to any textile library and should be carefully examined by every progressive colorist. To those interested in textile coloring, though unfamiliar with the German language, a perusal of this book will prove of value, on account of the numerous and excellent illustrations which it contains.

L. A. OLNEY

UNTERSUCHUNG UND NACHWEIS ORGANISCHER FARBSTOFFE AUF SPECTRO-CHEMISCHEM WEGE. VON JAROSLAV FORMÁNEK, o. Professor an der k. k. Böhmischen Technischen Hochschule in Prag, unter Mitwirkung von DR. EUGEN GRANDMOUGIN, Professor an der Höheren Chemischen Schule in Mülhausen i/E. Berlin: Verlag von Julius Springer. Zweiter Teil. 1. Lieferung, 1911. S. 164 mit 6 lithographischen Tafeln. Preis, M. 10.00. 2. Lieferung, 1913. S. 165-366 mit 7 lithographischen Tafeln. Preis, M. 14.00.

The first 56 pages are devoted to the classification of organic dyestuffs. The remainder of the two parts of the book (310 pages) gives a description of the absorption spectra of a large number of dyestuffs in various solvents, following the accepted system of classification. The plates give a schematic and qualitative illustration of the data given in the tables. They are very useful in giving a picture of the system of classification.

Dyestuffs are divided into four main "natural" groups: the green (blue-green), the blue (green-blue, blue-violet and violet), the red (violet-red, yellow-red) and the yellow (orange-

yellow and brown) dyestuffs. The main groups are again subdivided. The tables of data include only the green, blue and red dyestuffs. At the end of each table is given a list of the dyestuffs arranged alphabetically. About 400 green, 1100 blue and 900 red compounds are described.

The problem of determining the kind of compound in a dyestuff is treated in detail throughout the following processes: the preparation of a solution of the dyestuff; the determination of the wave length of the absorption bands; the development of characteristic reactions; and the use of the author's tables. A section is devoted to mixtures of dyestuffs.

This treatise is well written and presents a well-classified mass of data on the absorption spectra of colored organic compounds. It should prove of inestimable value to chemists whose problems include the detection of the nature of organic coloring matter. Spectroscopy is greatly indebted to the extensive and careful work of J. Formánek.

W. W. STRONG

THE PRINCIPLES OF APPLIED ELECTROCHEMISTRY. By A. J. ALLMAND, D.Sc. Illustrated. New York: Longmans, Green & Co. London: Edward Arnold. 1912. pp. x + 547. Price, \$5.00.

Part One of this treatise consists mainly of a very satisfactory, if brief, outline of the theory of solutions, with special reference to the applications to various electrochemical processes. It is this feature which distinguishes the present text from most works in English on applied electrochemistry. The early chapters deal with equilibrium reactions, Faraday's laws, osmotic pressure, conductivity and dissociation, energy relations, electrolysis and polarization, cathodic and anodic processes, etc. These topics are necessarily discussed briefly, the author assuming on the part of the reader a knowledge of the fundamentals of chemistry and electricity. In thus emphasizing the theoretical side of the subject the present work marks a distinct advance over the usual practice in writing texts in English.

Part Two gives a description of the various technical processes of importance, including processes for the manufacture of numerous chemicals, such as hypochlorite, chlorates, alkali, permanganate, carborundum, carbon bisulphide, etc., and various electrometallurgical processes. Throughout this part the close relation between theory and practice is pointed out.

The book is distinctly pleasing and shows plainly that the author has spared no efforts to make it as free as possible from those imperfections which usually mark first editions. The chief regret which the reader feels is that metallurgical processes have not received more extended treatments, but this,

of course, could not have been done without materially increasing the size of the volume, already large.

B. F. LOVELACE

DIE OXYDATION DES AMMONIAKS ZU SALPETERSÄURE UND SALPETRIGERSÄURE. Von Prof. ED. DONATH und Ing.-Chemiker A. INDRA in Brünn. Mit 10 Abbildungen. Sammlung chemischer und chemisch-technischer Vorträge. Begründet von F. B. Ahrens; herausgegeben von Prof. W. Herz, Breslau. XIX Band, 4/6 Heft. Stuttgart: Verlag von Ferdinand Enke. 1913. pp. 108.

In this monograph the authors have given a fairly complete and satisfactory résumé of the literature relating to the sources of ammonia and the methods used commercially for the oxidation of ammonia to nitrous and nitric acids.

B. F. L.

CHEMICAL GERMAN. An Introduction to the Study of German Chemical Literature, including Rules of Nomenclature, Exercises for Practice and a Collection of Extracts from the Writings of German Chemists and Other Scientists and a Vocabulary of German Chemical Terms and Others Used in Technical Literature. By FRANCIS C. PHILLIPS, Professor of Chemistry in the University of Pittsburgh. Easton, Pa.: The Chemical Publishing Co. 1913. London: Williams & Norgate. pp. xi + 241. Price, \$2.00.

The present book "contains rules of nomenclature interspersed with exercises intended to illustrate the use of German chemical terms pertaining to general chemistry, inorganic and organic, and to the various processes of the laboratory. These are followed by a collection of extracts from the writings of noted German chemists, having in many cases direct bearing upon the history of chemistry. A vocabulary of the more common German terms used in chemistry will aid the student in his translations. The work is intended for students who have had at least a year of German and who have mastered the elements of chemistry." A list of abbreviations frequently found in German chemical literature is also given.

A student who has conscientiously worked his way through this book should find no difficulty in reading any German article bearing on chemistry. He will find himself also in possession of a most interesting collection of extracts which alone make the book well worth owning.

C. A. R.

THE 'WELLCOME' PHOTOGRAPHIC EXPOSURE RECORD AND DIARY. 1914. U. S. A. Edition. New York: Burroughs Wellcome and Co. pp. 280. Price, 50 cents.

Every owner of a camera should possess a copy of this beautifully gotten up and useful little book.

"It condenses into one small volume clear, definite and precise instructions on a very wide range of subjects. All the little wrinkles and dodges which long experience has taught the successful worker are here analyzed and set forth in simple formulas and exact directions such as help the beginner and

serve as a useful reminder to the expert. Development, toning, fixing, printing, the various processes of production in warm tones and colors, and the methods of dealing with errors of technique are explained, particular attention being directed in the 1914 edition to the green and blue toning, and the production of various colors by development and other methods. On the subject of exposure this book is the last word, containing, in addition to its light tables for each month and factors for plates and films, the special device attached to the cover which tells the correct exposure at one turn of the disc." It is provided with blank ruled pages to record negative and positive exposures and for daily memoranda, and is substantially and tastefully bound in red cloth. It should prove a "Wellcome" gift to any camera enthusiast.

C. A. R.

A NEW ERA IN CHEMISTRY. Some of the More Important Developments in General Chemistry during the Last Quarter of a Century. By HARRY C. JONES. New York: D. Van Nostrand Company. 1913. pp. xii + 326. Price, \$2.00.

Any book from the pen of Professor Jones is welcome, and no book more acceptable than a review of modern chemistry from his standpoint, regarding which he could write as few others, "quorum pars fui." Then his own enthusiasm for his subject is so great that it cannot fail to be contagious, and even abstruse topics in physical chemistry become as entertaining as romance; indeed in the author's hands much of the history of modern chemistry is a real romance, romance of fact more entrancing than any romance of fiction.

The purpose of the book is laid down in the preface: "It is, however, clearly recognized that there is a difference between the chemistry of twenty-five years ago and that of today. That this is really a difference in kind is not always clearly understood by those who have watched the development during that period, or by those who have not studied chemistry long enough to have the necessary perspective. It has seemed desirable to point out as clearly as possible in what this difference consists; how these new developments were brought about and by whom. This is the object of this little work. My apology for adding another book to the literature of chemistry is that I have lived during the 'New Era,' have known well most of the men who have been instrumental in bringing it about, and have been a student of the three leaders in this movement—Van't Hoff, Arrhenius and Ostwald." And it is this personal element which lends such a charm to the book.

The first chapter is entitled "Condition of Chemistry in

1887," and is a brief résumé of chemical history up to that time, with the emphasis well put on the salient points. The author's viewpoint is made clear by his characterization of the period up to 1887 as the "fact discovering" or "brick making" period, "very important in itself and absolutely essential to the subsequent development of a science of chemistry." "It was, however, not a science of chemistry," but a system. The year 1887 marks roughly "the beginning of the transition from a system into a science of chemistry." Of course, there are those who might differ from this opinion and incline to the view that there was at least the beginning of a chemical science at an earlier period; indeed, some of us thought that we were engaged in studying science as we listened to the lectures of Wöhler and Hofmann and worked in the laboratory under Hübner and Tiemann and Liebreich, and surely we were just as happy over it as if we had been doing *real* scientific work under Ostwald and Nernst; I must admit, though, that there would have been more real enthusiastic inspiration under the genial author of this book, and in view of this enthusiasm we can pardon his strong partiality for modern chemical science.

The next chapters trace the development of the law of mass action, up to the work of Guldberg and Waage; the thermochemical work of Thomsen, Hess and Berthelot; the development of stereochemistry by van't Hoff, Pasteur, LeBel and Guye; the phase rule of Willard Gibbs. And here we must pause to quote the last paragraph of this chapter: "Looking at the Phase Rule in as broad and impartial a manner as possible, I am unable to get away from the thought that by certain men it has been an overridden hobby." We wonder if there are not other phases of modern chemical science which might be classed as overridden hobbies; and yet in their masters' eyes they are beautiful steeds.

I doubt if the subjects of osmotic pressure and electrolytic dissociation have ever been as completely, succinctly and withal attractively treated as in the 60 pages of this book devoted to them. The vividness of description may be judged by the following: "I have seen the following experiment performed. Pure, dry sulphuric acid in a tube, and a piece of very carefully dried metallic sodium plunged into it. The sodium remained suspended in the acid just as quiescently as it would in ligroin." Surely pages of statement would less effectively illustrate the rôle of water.

Not least in interest or in importance is the chapter on the solvate theory of solution, for here we have Jones's own work set forth with conclusive logic. It has been his task to apply the theories of ideal solutions to the actual solutions one meets

in the laboratory and in every-day life, and hence he has given us "a theory of solutions in the broad sense of that term."

To the work of Ostwald and his students and co-workers (shall we be considered purists if we object to the unhyphenated "coworkers"?) are devoted the two longest chapters of the book. We are forced to agree with our author in his enthusiastic admiration of his great, many-sided teacher. If Ostwald did not create modern chemical science, he at least compelled the universal recognition of the fact that it is a science, however narrowly one may define the word. In this connection is treated the work of Beckmann, of Nernst, of LeBlanc, of Bredig, of A. A. Noyes, of Richards, and of others who have been leaders of the modern era.

The last chapter is devoted to the Electron and Radiochemistry, an excellent recapitulation of the development of this field, brought down to the present day. The book concludes with an appendix containing charming personal impressions and reminiscences of Mendeléeff, Kekulé, Gibbs, Ramsay, van't Hoff, Arrhenius, and, above all, Ostwald. May we again quote: "A visit of a day to Ostwald at Gross-Bothen is worth a trans-Atlantic trip. You cannot be in his presence for ten minutes without realizing that you are facing a really great man. His breadth of knowledge, his depth of interest, his unbiased judgment of men and ideas, his originality and many-sidedness, all taken together, make him one of the most interesting personalities of the age. * * * * He has lived to see chemistry largely transformed from empiricism and system into science, due in no small measure to his own organizing power. An original and systematic mind, a kindly and generous heart, a many-sided genius is Wilhelm Ostwald."

Verbum sat. No chemist, be he teacher, student or technologist, should fail to read this book, whether to learn for the first time what modern chemistry is doing, or to review systematically what he already knows but in disjointed sections, or merely to while away a few leisure hours in reminiscing over his own work. As a whole, the book comes pretty near being a philosophy of modern chemistry.

JAS. LEWIS HOWE

THE SYNTHETIC DYESTUFFS AND THE INTERMEDIATE PRODUCTS FROM WHICH THEY ARE DERIVED. By JOHN CANNELL CAIN, D.Sc. (Manchester and Tübingen), Editor of the *Journal of the Chemical Society*, Examiner in Coal Tar Coloring Matters to the City and Guilds of London Institute, and JOCELYN FIELD THORPE, D.Sc. (Manchester), Ph.D. (Heidelberg), F.R.S., F.I.C., Sorby Research Fellow of the Royal Society, Late Lecturer on Coloring Matters in the University of Manchester. Second Edition, Revised. London: Charles Griffin & Company, Limited. 1913. pp. xvii + 1423. Price, 16s.

This book is a most excellent treatise on this difficult and

complicated chapter of organic chemistry. It is divided into the following four parts: Theoretical, Practical, Analytical, and Appendix, containing tables of specific gravities of solutions, etc. The theoretical part contains a discussion of coal tar, and the various classes of intermediate products, and 16 chapters devoted to the dyes themselves. The practical part gives a description of the technical laboratory and the preparation of the intermediate products and the dyestuffs themselves. The analytical part gives the analytical methods, the behavior of the principal fibers toward dyes, and the reactions of the dyes on the fiber. The text is clear and the use of graphical formulas is a great aid in the presentation of the subject.

S. F. A.

COURS DE CHIMIE ORGANIQUE. Par FRÉD. SWARTS, Professeur à l'Université de Gand, Membre de l'Académie Royale de Belgique. 2^e édition revue et augmentée. Avec figures. Paris: A. Hermann & Fils; Gand: Ad. Haste. 1913. pp. vi + 754. Price, Fr. 15.00.

The second edition of this book is a general treatise on organic chemistry, suitable for college students. The arrangement is good, the text is clear, and the use of graphical formulas is commendable.

S. F. A.

RECENT ADVANCES IN ORGANIC CHEMISTRY. By A. W. STEWART, D.Sc., Lecturer on Organic Chemistry in the Queen's University, Belfast. With an Introduction by J. NORMAN COLLIE, Ph.D., LL.D., F.R.S., Professor of Organic Chemistry in University College, London. Second Edition. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1911. pp. xv + 320. Price, \$2.50, net.

The second edition of this well-known and excellent treatise still imbues the reader with the spirit of the rapid progress made to-day in the theories of organic chemistry. The chapters on the Grignard reaction and the chemical action of light have been replaced by a chapter on quinoles and another on the triphenylmethyl problem. The book deals with such important chapters as the polymethylenes, the terpenes, the alkaloids, the purines, the polypeptides, the polyketides, the quinoles and the triphenylmethyl question, each of which is treated in a thorough way.

S. F. A.

TABELLE DER WICHTIGSTEN ORGANISCHEN VERBINDUNGEN, geordnet nach Schmelzpunkten. Zusammengestellt von DR. RICHARD KEMPF, Assistent am Königl. Materialprüfungsamt zu Berlin-Lichterfelde. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1913. pp. xi + 135. Price, M. 8.80.

The title shows the object of this author in writing, or, rather compiling, this little book. About 2500 of the most common compounds are characterized in this volume by the melting point, color, boiling point, name, graphical formula,

and by the citation to the original literature and to Beilstein. Although its range is too limited, it should prove very useful as a handbook.

S. F. A.

METALLURGICAL ANALYSIS. By NATHANIEL WRIGHT LORD, Late Professor of Metallurgy and Mineralogy, Ohio State University, and DANA J. DEMOREST, Professor of Metallurgy, Ohio State University. Third Edition. International Chemical Series, H. P. TALBOT, PH.D., Consulting Editor. New York: McGraw-Hill Book Co., Inc. 1913. pp. xvii + 334. Price, \$2.50.

This book was originally issued in 1893 as a small volume of 100 pages, the second and enlarged edition being published ten years later, and now comes this third edition "re-written so as to incorporate in the old methods the recent advances in knowledge bearing on them." "Also many new subjects have been added so as to include in the book practically all the methods likely to be used by the metallurgical chemist."

The book was originally intended for the use of the late Professor Lord's students, but in its second and third editions it has grown away from the student or teaching point of view and the more technical side has been developed. In this development the book has undoubtedly suffered from growing pains and it consequently appears very uneven in character. Evidently the attempt has been made to include everything necessary for the worker in the metallurgical field, without reference to previous training, and little is left to the imagination. Original imperfections have been transmitted, and many others added, in this edition. The English in places is distinctly of the busy, commercial laboratory type where results are of first importance and manner of presentation an unimportant detail. There is, in places, an uncertainty of statement which would be particularly annoying to the earnest student, such as "water is said to decompose the precipitate to a slight extent," "the phosphoric acid is also said to prevent the reduction of the permanganate by HCl," "*probably* contains a complex compound," "*perhaps* as $\text{Fe}_2\text{Cl}_2(\text{OH})_2$," "*changes principally* to Mn_2O_4 ." The untrained will not care about the real truth, but others will want to know.

Some preliminary knowledge of quantitative analysis is assumed, but if the worker is weak on calculations he may get his results by following directions and making a proportion but he will have learned little about principles involved. Instead of insisting on always weighing "factor weights" and multiplying by some decimal number to get percentages, it would have been much preferable to have explained the principles once for all. There is, to be sure, a chapter of two pages

at the end of the book on "Calculation of Normal Solutions," which is, if the subject is to be treated at all, badly placed and inadequate. In some places the weighed precipitate is said to contain a certain percentage of the element desired, and again such statements as this, referring to $Mg_2P_2O_7$, "this contains 0.279 of phosphorus." There is much unevenness of this character in dealing with calculations.

In each chapter there is a description of the method employed, and this is preceded in all cases by a statement of principles and in most cases by a series of notes bearing upon the methods. A much more logical treatment of the subject would have been to have given the procedure first and then have the notes follow the method. This is particularly objectionable from a teacher's point of view, as the discussion of the method is given before the student knows anything of the process employed.

The book is essentially a collection of methods in ferrous and non-ferrous metallurgy covering a wide field and containing much excellent material but very poorly digested and not very logically treated.

H. F.

LIQUID AIR, OXYGEN, NITROGEN. By GEORGES CLAUDE, Engineer Laureate of the Institute of France. English Edition, Corrected and Brought up to Date by the Author. Translated by HENRY E. P. CORTRELL, Assoc. M.I.C.E., M.S.C.I., F.R.C.I. With a Preface by d'ARSONVAL, Member of the Institute of France. Philadelphia: P. Blakiston's Son & Co. 1913: pp. xxv + 418. Price, \$5.50.

This book is a treatise on the liquefaction of gases, with special reference to the author's own application of theory to the production of liquid air, oxygen and nitrogen, the latter by partial condensation. While other processes are given, the successful development of Claude's method of expansion with external work is most fully and graphically described.

The book is divided into four parts: Part I, on Liquefaction of Gases, is a historical résumé of the subject, down to the liquefaction of helium. Part II, on The Commercial Liquefaction of Air, is largely a theoretical discussion and comparison of the two methods of expansion, with or without external work. Part III is on the Preservation and Properties of Liquid Air, and may well be in the original a verbatim report of the author's lectures, in such popular and entertaining style is it written. Part IV, on The Separation of the Air into Its Elements, is the most original portion of the book, and describes and discusses the various methods, theoretical and in practical use, for the commercial production of oxygen and nitrogen from the air. The last chapter enumerates, with illustrations, the principal plants having Linde installations as well as those of Claude.

More than 150 illustrations are used in the book, which is most attractively gotten up, and is valuable for reading as well as for reference. The translation is calculated to mar one's enjoyment of the book, so poorly is it done. J. L. H.

ÜBER NATRONZELLSTOFF, seine Herstellung und chemischen Eigenschaften.
Von DR. ING. CHRISTIAN CHRISTIANSEN, Diplomingenieur. Schriften
des Vereins der Zellstoff- und Papier-Chemiker. Heft 6. Berlin:
Verlag von Gebrüder Borntraeger. 1913. pp. 154. Price, M. 5.00.

This monograph on the soda cellulose process consists of 133 pages of subject matter and an appendix of 11 pages which gives a chronological list of references to the patent and general literature.

The first 59 pages take up a historical review of the various alkaline processes, the composition and utilization of the waste liquors, recent technical accomplishments, the recovery of alkali, the control of manufacturing conditions and the theory of cooking. This portion of the work is fairly well covered though the author does not quote from actual manufacturing results as much as would seem desirable and also distinctly avoids an expression of personal opinion. On the whole, it may be said of this part of the work that it contains little which will be new to the man who is well up in the chemistry of the process though it may be of material assistance to the rule-of-thumb man.

The remainder of the monograph is given over to experimental work and a discussion of its results, starting with an outline of the work and continuing with a discussion of the course of the soda process, the relation between alkali consumption, yield, properties of the cellulose, etc., and suggesting technical applications and methods of controlling the cooking process. Tables are given showing the cooking results as well as the chemical constants of the various pulps, as copper number, hydrolysis number, resin and wood gum determinations, etc. Curves for a number of cooks are also given which show the relations of a number of the important factors and lay particular stress on the periods during which the consumption of caustic soda ceases. Finally there are detailed descriptions of 24 cooks made in a jacketed digester by the straight soda process, and details of the methods employed in testing the fiber produced.

The experimental work involved was large in amount and appears to have been carried out with great care, yet certain facts render the results of less value than they should be. No statement is made of the kind of wood used, the conclusions are drawn from very small differences in yield and appearance

and the location and duration of the constant points depend on the analyses of samples of 1 cc. of black liquor by a titration method which is not of the highest accuracy. The method of calculating the proportion of alkali is also given, yet when one recalculates the figures given in the detailed cooks 16 out of 24 are not found to correspond to the numbers published. In the case of Cook 1 the yield given on p. 96 is 67 per cent. while in the table on p. 64 it is given as 75 per cent.

In spite of these criticisms the reviewer considers this work to be valuable because of the way in which the subject has been approached and because it is suggestive of an immense amount of work which it seems desirable to perform. The book can be read to advantage by all who are interested in the scientific control of the soda process but will prove of somewhat less interest to those working by the sulphate process.

E. SUTERMEISTER

AN INTRODUCTION TO THE CHEMISTRY OF PLANT PRODUCTS. By PAUL HAAS, D.Sc., Ph.D., Lecturer on Chemistry, Royal Gardens, Kew, Demonstrator of Chemistry and Toxicology in the Medical School of St. Thomas's Hospital, London, and T. G. HILL, A.R.C.S., F.L.S., Reader in Vegetable Physiology in the University of London, University College. With diagrams. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1913. pp. xii + 401. Price, \$2.25.

The title of this book is possibly not the most appropriate one which could have been devised. The reviewer, at any rate, was surprised to find that the volume dealt with the chemistry of plants from a physiological rather than from a technological standpoint. The authors announce that their work was written in order to provide students of plant physiology with an account of the chemistry and significance in metabolism of the more important compounds found in plants. They have filled a real want, for no other work in English, good or bad, even approximately covers the same ground. Their treatment of the subject is in no sense encyclopedic, since it is intended rather to orient the student in a difficult field than to take the place of a work of reference such as Czapek's "Biochemie der Pflanzen." Only those compounds are treated which are of general occurrence or of special physiological importance in plants. A knowledge of elementary chemistry on the part of the reader is presupposed—otherwise the essentials of the subject could not have been brought within the convenient compass of 400 pages.

Notwithstanding the fact that most of the problems of plant physiology have to be attacked by chemical methods, there is not a university in this country where a good course in plant physiology is supplemented by adequate training in plant

chemistry. Nevertheless, there is a continued demand for men to fill positions which require combined chemical and botanical training. To many students, therefore, Haas and Hill's book may be cordially recommended as a substitute for college courses which do not exist. It may be hoped, moreover, that the chemical departments of some of our universities will be encouraged by the appearance of so excellent a text-book to provide a course in biochemistry which will interlock, on the one hand, with the courses in plant physiology and on the other with the courses in organic and physical chemistry.

From the standpoint of either student or teacher, the book leaves little to be desired. The nine chapters correspond in general to the main groups of compounds which occur in plants. Each chapter presents a classification of the compounds which it includes, treats the more important members in some detail, often giving the methods for their quantitative estimation, and points out their physiological significance. The numerous bibliographic footnotes are especially to be commended.

H. H. BARTLETT

ELEMENTS OF WATER BACTERIOLOGY, with Special Reference to Sanitary Water Analysis. By SAMUEL CATE PRESCOTT, Associate Professor of Microbiology in the Massachusetts Institute of Technology, and CHARLES EDWARD AMORY WINSLOW, Associate Professor of Biology, College of the City of New York, and Curator of Public Health, American Museum of Natural History, New York. Third Edition, Rewritten. New York: John Wiley & Sons, Inc. 1913. pp. xiv + 318. Price, \$1.75.

Since the first edition of Prescott and Winslow's little book on water bacteriology the publications on this subject have become more and more important both in America and in Europe. The literature is now so extensive that it would seem well nigh impossible for any one book to present it properly and at the same time with reasonable brevity. In this third edition of their text-book, which is in reality the second edition rewritten, Prescott and Winslow have attempted this task and have, we believe, done it successfully. As a necessary consequence, this edition is much enlarged, comprising now some 300 pages divided into twelve chapters. One of these chapters is devoted to shell-fish examination, an important addition and one especially welcome at the present time when the question of sewage pollution of shell-fish is so important. The principal facts and conclusions of earlier editions are brought out in the new one with, however, more elaborate discussion than formerly. In the main, the earlier conclusions as to the value of careful bacteriological analysis of water from a sanitary

standpoint are adhered to and the authors still believe, as do the majority of American bacteriologists, that the isolation of intestinal bacteria from small quantities of water is the most valuable sign we have of sewage pollution. They also maintain their former position as to the superiority of bacterial counts of water made on gelatin at room temperature over those made on agar at the body temperature, but are inclined to admit that the latter procedure gives more valuable information than was originally supposed. In one important particular this edition differs from the earlier ones inasmuch as the authors have here adopted a new definition for the colon group of organisms. According to them "the colon group may be defined as including all aerobic non-spore-forming bacilli which produce acid and gas in dextrose and lactose media." In thus broadly defining this group of bacteria, Prescott and Winslow have departed from classical procedures and dogmas and it will be very interesting to see whether bacteriologists in America will follow them in their position. In this connection it should be pointed out that water has heretofore been condemned from a sanitary standpoint on the basis of finding in it a specific microorganism which is the predominant species in the human dejecta, namely, *Bacillus coli* of Escherich. Bacteriologists are in the main agreed about the cultural reactions of this species which were clearly and definitely given by the investigator who first carefully studied it and gave it its accepted name, although it must be admitted that the original description of this species has not been rigidly adhered to by subsequent workers. The isolation of this organism from water is of great value and, indeed, is the most delicate test we have at the present time for sewage pollution. As now defined by Prescott and Winslow, the colon group will comprise not only all organisms with the reactions of *Bacillus coli* but a variety of bacteria which differ from it in certain cultural features which have always been regarded as of specific value in the classification of bacteria. Such organisms were described years ago by Eisenberg, for instance, and named by him *Bacillus liquefaciens*, and attention has been directed to them by a number of observers abroad and in this country. They are not the *Bacillus coli* of Escherich. Such organisms might be included in the colon group on a broad basis but they have been isolated from the human dejecta only on rare occasions and while their presence in water may indicate sewage pollution, the point is not yet proved with such a degree of certainty as to justify the condemnation of water on this basis alone. There are in addition certain organisms widely distributed in nature in decaying vegetation, for instance, as the various species of the

proteus group (*Bacillus proteus vulgaris* of Hauser) which produce acid and gas in dextrose and lactose media. The isolation of such organisms from spring water could hardly have a sanitary significance and yet they would be included in the colon group according to this definition. We are inclined to believe with the present evidence that the adoption of this broad definition of the colon group as given by Prescott and Winslow is likely to rob the colon test of some of its value without any corresponding benefit. Future experience will determine this point. In other respects this last edition represents a great improvement over earlier editions and can be most highly recommended to all students of Hygiene and Sanitation.

W. W. FORD

THE EXAMINATION OF WATERS AND WATER SUPPLIES. By JOHN C. THRESH, D.Sc., M.D. (VIC.), D.P.H. (CAMBR.). Second Edition, with 53 Illustrations. Philadelphia: P. Blakiston's Son & Co. 1913. pp. xx + 664. Price, \$5.00.

The present edition of this standard work has been entirely revised and enlarged and several new chapters added. The book is divided into three parts: The first discusses the examination of sources of supply, something too often neglected by water analysts, and points out the possibilities of contamination corresponding to the various sources. The description of the uses of dyes, other chemicals and bacteria in detecting polluting sources is particularly interesting. Dr. Thresh's wide experience has given him an abundance of material for illustrations.

The second part deals with the interpretation of results of the chemical, microscopical and bacteriological examinations. In general, the interpretations and figures given will apply to waters in this country—the chlorine values being exceptions, as we rarely find good waters of such high chlorine content as recorded for England. Figures are given to show that smaller amounts of sewage pollution may be detected by bacteriological methods than by chemical, although the importance of the former method is somewhat lessened by the fact that empirical standards are often misleading. The author classifies waters from the bacteriological standpoint, on the basis of the presence or absence of *B. coli* in 100 cc. and spores of *B. enteriditis sporogenes* in 250 cc.

The third part gives the methods of analysis—chemical, microscopical and bacteriological—which are in use in his laboratory. These vary somewhat from the methods in use in this country. On account of recent discussions it is interesting to note that Dr. Thresh makes bacterial counts both at

20° C. and at 37° C. Records of a large number of analyses and some 36 plates illustrating the microscopical analysis of water are given.

The appendix contains methods of preparing solutions and a number of useful tables.

The book is the most complete work published on the subject, and this revision is a welcome addition to the literature of water analysis.

JOHN F. NORTON

TRAITÉ DE CHIMIE MINÉRALE. Par H. ERDMANN. Directeur de l'Institut de Chimie Minérale de la Technische Hochschule de Berlin. Ouvrage traduit sur la 5^e édition allemande par A. CORVISY, Professeur Agrégé des Sciences Physiques au Lycée Gay-Lussac, Professeur Suppléant à l'École de Médecine et de Pharmacie de Limoges. Tome second: Étude des Métaux. Avec 76 figures et trois planches spectrales en couleurs. Paris: Librairie Scientifique A. Hermann et Fils. 1914. pp. 331. Price, Fr. 10.00.

The present book is the second and concluding volume of Corvisy's excellent translation of Erdmann's "*Lehrbuch der anorganischen Chemie*," the appearance of the first volume of which has already been noted in *THIS JOURNAL*.¹

LES PROGRÈS DE LA CHIMIE IN 1912. Traduction française autorisée des "Annual Reports on the Progress of Chemistry for 1912, Vol. IX, issued by THE CHEMICAL SOCIETY, LONDON," et publiée sur l'initiative du Service de Recherches du Laboratoire Municipal de Paris. Traducteurs: MM. D. FLORENTIN, Chimiste au Laboratoire Municipal; E. GELIN, Chimiste contrôleur au Laboratoire Municipal; P. HUCHET, Licencié ès-Sciences, Préparateur au Laboratoire Municipal; M. DRECO, Chef des Travaux de Physique à l'École de Physique et de Chimie de Paris; J. SAPHORES, Chef des Travaux de Physique à l'École de Physique et de Chimie de Paris; P. POURQUERY, Ingénieur-Chimiste, I. C. A. Paris: Librairie Scientifique A. Hermann et Fils. 1913. pp. xiv. + 411. Price, Fr. 7.50.

In the preface to this translation, Dr. André Kling, director of the Paris Municipal Laboratory, points out the need, in these days, of ever increasing complexity in the science of chemistry and the consequent necessity of narrower and narrower specialization by the individual worker, of some book that will bring before the chemist the gist of the more important work being done in other than his own special field. He then goes on to say: "In France, except for the Reviews of Chemistry, to which certain journals annually devote some pages, we have no such publication. And we cannot help being surprised at this lack when we consider that the French spirit is especially adapted to the realization of works of this kind, the object of which is to present in clear and concise form ideas confusedly buried in the prolixity of certain original memoirs.

¹ Vol. 50, p. 132.

... The reason for this lack is of purely commercial origin, and if I have been compelled, for the present, to give up the idea of publishing, with the collaboration of specialists chosen from the various branches of chemistry, an Annual Review of the facts and ideas in chemistry, it has not been because I have been unable to find the men with the necessary ability and good-will, but simply on account of the hesitation of publishers, troubled by the crisis through which the French scientific book has passed." Being unable to bring out an original publication, Dr. Kling decided to offer his fellow-chemists speaking the French language a translation of a foreign book and his choice at once fell on the Annual Reports of the London Chemical Society. If the present volume meets with an encouraging reception, these Reports will be translated annually.

C. A. R.

NEUERE ANSCHAUUNGEN AUF DEM GEBIETE DER ANORGANISCHEN CHEMIE. VON PROF. DR. A. WERNER in Zürich. Dritte durchgesehene und vermehrte Auflage. Die Wissenschaft. Sammlung von Einzeldarstellungen aus den Gebieten der Naturwissenschaft und der Technik. Band 8. Braunschweig: Druck und Verlag von Friedr. Vieweg und Sohn. 1913. pp. 419. Price, M. 12.00.

The "Neuere Anschauungen" of Werner is so well known that it would be superfluous to do more here than call attention to the appearance of the third enlarged edition.

H. C. J.

INTRODUCTION À LA CHIMIE DES COMPLEXES. Théorie et systématique de la chimie des complexes minéraux. Par G. URBAIN et A. SÉNÉCHAL. Paris: Librairie Scientifique A. Hermann et Fils. 1913. pp. 477. Price, Fr. 15.

We read in the preface that "every chemical compound, whose formula contains a large number of atoms, should be called a complex. If we therefore except the elements and binary compounds of these with one another, the study of complexes is coextensive with that of chemistry itself."

One other section of the preface calls for special comment. The authors call attention to the tendency to-day of making everything practical. The results of an investigation are frequently regarded as of value just in proportion to the possibility of applying them to some useful end. The authors express their own minds on this point without any ambiguity. "We do not believe that the chemist can subscribe to this point of view. Science can and ought to exist independently of all industrial questions. It would be an era of decadence if all effort were considered sterile, and all investigations in vain, which did not have an immediate practical end." "We have on this point a profound conviction. The best service which

the man of science can render to the engineer is to coordinate the science from which the engineer is to obtain profit, is to perfect the methods of reasoning and to establish the relations between cause and effect." This is really refreshing at a time when the "idealism" of the past seems on the wane, especially in those very quarters where we should least expect it to decay. The laboratory of the true man of science must be kept 180 degrees from the patent office in the future, as in the past, if science is to accomplish its highest good for mankind.

The book is divided into four parts of several chapters each. These are: Part I, Generalities; Part II, Perfect Electrolytic Complexes; Part III, Imperfect Complexes; and Part IV, Double Salts.

Any book on the subject of general inorganic chemistry from the pen of Urbain is welcome, because it comes from a leading investigator in this field—from a real master. H. C. J.

NOTIONS FONDAMENTALES DE CHIMIE ORGANIQUE. Par CHARLES MOUREU, Membre de Institut et de l'Académie de Médecine, Professeur à l'École supérieure de Pharmacie de l'Université de Paris. Quatrième édition, revue et mise au courant des derniers travaux. Paris: Gauthier-Villars. 1913.

The author has combined in this book both a text and a résumé of the recent progress in organic chemistry. The details concerning boiling points, specific gravities, etc., are omitted to a large extent, and the broader aspects of methods of preparation and interrelation of classes are given more attention. Such newer chapters as the Grignard methods, the reductions in alcohols in the sunlight discovered by Ciamician and Silber, etc., are given much more fully than usual. The book has much of interest and importance not ordinarily seen in texts.
S. F. A.

ANLEITUNG ZUR DARSTELLUNG PHYTOCHEMISCHER UEBUNGSPRÄPARATE für Pharmazeuten, Chemiker, Technologen u. a. Von Dr. D. H. WESTER. Mit 59 Textfiguren. Berlin: Verlag von Julius Springer. 1913. pp. xi + 129. Price, M. 3.60; bound, M. 4.20.

The excellent little book has, first, a very complete section on the technique required of pharmacists and chemists, the description of the apparatus being especially good. In the second part is given a list of preparations, including sugars, terpenes, tannins, alkaloids, enzymes, proteids, glucosides, waxes, fats, acids and alcohols. While the directions for the preparations are very good, the reactions are not discussed as fully as desirable.
S. F. A.

TABLES ANNUELLES DE CONSTANTES ET DONNÉES NUMÉRIQUES DE CHIMIE, DE PHYSIQUE ET DE TECHNOLOGIE. Publiées sous le patronage de l'Association Internationale des Académies par le Comité International nommé par le VIIe Congrès de Chimie appliquée (Londres, 2 juin, 1909). Volume II, Année 1911. Paris: Gauthier-Villars; Leipzig: Akademische Verlagsgesellschaft m. b. H.; London: J. & A. Churchill; Chicago: University of Chicago Press. 1913. pp. xl + 759.

This volume of physical constants should be accessible to every chemist interested in the quantitative aspect of chemical science. The accumulation of data is progressing so rapidly that it is practically impossible to read even the important articles, and difficult to remember just where to find certain facts desired. This book gives all the important data of 1911, in about 50 subjects, such as reaction velocities, conductivities, colloids, engineering, magnetism, essential oils, animal physiology, and organic chemistry. A personal letter from Mons. Marie to the reviewer indicates that more aid should be given the International Committee in order to allow the succeeding volumes to appear more promptly.

S. F. A.

SMOKE. A Study of Town Air. By JULIUS B. COHEN, Ph.D., B.Sc., F.R.S., Professor of Organic Chemistry in the University of Leeds, and ARTHUR G. RUSTON, B.A., B.Sc., Science Tutor in the Department of Agriculture, University of Leeds. Illustrated. New York: Longmans, Green and Co.; London: Edward Arnold. pp. 88. Price, \$1.40.

This small volume contains a considerable amount of very valuable material which the authors have obtained as a result of their own investigations of certain of the evils which result from the incomplete combustion of soft coal. These results are presented in a very clear style and the illustrations are excellent. Some very valuable material is presented on the effects of soot and sulphuric acid contained in smoke-polluted atmospheres upon the growth of vegetation and the corrosion of masonry and metal work. There is also included an appendix by Dr. Ascher on "The Influence of Coal-Smoke upon the Health."

The authors have confined their work to the study of the nature and quantity of soot in the air and the injurious effects of soot and sulphuric acid, without taking up the causes which produce smoke or methods for its abatement. Neither have the authors presented any data of their own upon the loss of heat which results from the incomplete combustion of coal of which smoke is an indication.

The book should be of considerable value to those interested in the question of smoke and its injurious effects. J. C. W. F.

HANDBUCH DER ARBEITSMETHODEN IN DER ANORGANISCHEN CHEMIE. Herausgegeben von DR. ARTHUR STÄHLER, Privatdozent an der Universität Berlin. Erster Band. Mit zahlreichen Abbildungen und Tabellen. Leipzig: Verlag von Veit & Co. 1913. S. xii + 742. Preis, M. 25.00; geb., M. 28.00.

This is the first of five volumes which are to constitute the completed *Handbuch* of the above title. It will be seen at once that the work is to be an extensive treatise, as the first volume contains 786 pages and is very profusely illustrated, which adds very much to its value.

It is not possible to attempt to review such a work as this with only one volume at hand, but the names of the fifty-eight well-known authors who are writing this *Handbuch* assure the value of the work when completed. It will be specially valuable as there is no work of recent date which treats this broad subject at all thoroughly, and the subject treated renders it equally useful to scientific and industrial laboratories.

The general arrangement of the five volumes is as follows: *Allgemeiner Teil*, Band I. Das anorganisch-chemische Laboratorium und seine Ausstattung—Mechanische Operationen. Band II. Physikalische und chemische Operationen und Hilfsoperationen. Band III. Physikochemische Bestimmungen. *Spezieller Teil*. Band IV. A. Körperklassen. B. Elementen und Verbindungen der Gruppen 1-3. Band V. Elemente und Verbindungen der Gruppen 4-8—Register.

A brief outline of the contents of Vol. 1 is as follows:

The inorganic chemical laboratory and its equipment. The structural arrangement of the inorganic chemical laboratory (Alfred Stock). Objects for the equipment of the laboratory (Stähler, Groschuff, J. Bronn). Electrical equipment (Günther Schulze, Stähler). Heating and cooling arrangements (E. Schirm, Stähler, J. v. Wartenberg, J. Bronn, L. Weiss). General precautions for laboratory work (Stähler). Mechanical operations (Stähler, T. W. Richards). Assembling of apparatus. General operations.

The publishers state that the whole work will be completed within two years from the time of announcement. J. C. W. F.

TRAITÉ COMPLET D'ANALYSE CHIMIQUE APPLIQUÉE AUX ESSAIS INDUSTRIELS. Par J. POST, Professeur honoraire à l'Université de Goettingue, et B. NEUMANN, Professeur à la Technische Hochschule de Darmstadt. Avec la collaboration de nombreux chimistes et spécialistes. Deuxième édition française entièrement refondue. Traduite d'après la troisième édition allemande et augmentée de nombreuses additions par G. CHENU, ING. E. P. C., Licencié os sciences, et M. PELLET, ING. I. N. A., Licencié os sciences Tome troisième, second fascicule. Goudron de houille, Matières colorantes. Avec 8 figures hors le texte. Paris: Librairie scientifique A. Hermann et Fils. 1913. pp. 465-902. Price, Fr. 15.00.

The book is a good translation of the fourth part of the

second volume of the third German edition of Post's "Chemisch-technische Analyse," or that section of this well-known handbook on methods of chemico-technical analysis in which Prof. G. Schultz has dealt with coal tar, the mineral pigments, the natural and synthetic dyestuffs, and the color lakes, and which was lately reviewed in *THIS JOURNAL*.¹ The "numerous additions" mentioned on the title page evidently have reference to the new matter introduced by Prof. Schultz rather than to any considerable additions to the text made by the French translators.

S. P. MULLIKEN

TECHNICAL GAS AND FUEL ANALYSIS. BY ALFRED H. WHITE, Professor of Chemical Engineering, University of Michigan. International Chemical Series: H. P. TALBOT, Ph.D., Consulting Editor. New York: McGraw-Hill Book Company, Inc. 1913. pp. x + 276. Price, \$2.00.

The author states in his preface that he has aimed in this book to present the conclusions of certain official committees and government bureaus which he names, and to indicate where there has been marked dissent from them. The work is more than a compilation, however, since it includes much valuable material derived from the author's own wide experience in the field of gas and fuel testing. There are 12 chapters (173 pp.) devoted to gas, one chapter (8 pp.) to liquid fuels, and 4 chapters (65 pp.) to coal. In view of the relatively great industrial importance of coal and the widespread efforts to increase efficiency in its use, and also in view of the rapidly increasing use of liquid fuels in modern industry, it seems that the author has unduly subordinated these two subjects to that of gas in a work on general fuel analysis.

The book is well suited to the use of engineering students or technical chemists who do not require the highest attainable degree of accuracy. The one chapter given on exact gas analysis is incomplete and might better have been omitted in a work of this character. This chapter presents some inexact methods, such as the use of Hempel pipettes with make-and-break connections, and the explosion method for methane and hydrogen, while omitting any description of the Haldane or Burrell apparatus for minute quantities of carbon dioxide and methane or of apparatus for analysis at constant volume. For students' use the book is perhaps lacking in explanation of underlying scientific principles; the inadequate treatment in Chapter I of the subject of solubility of gases in water and the effect of this on the accuracy of gas analysis is an example of this tendency. Chapter V on earlier types of apparatus is of no value to any one but a student of the history of the subject.

There are excellent chapters on the heating value and the

¹ Vol. 44, p. 563.

candle power of gas and on the heating value of coal. Full descriptions, well illustrated, are given of various types of calorimeters and photometers, with ample and most useful explanations of sources of error and their relative importance. Sampling of coal is given a separate chapter and is treated thoroughly and well—much better than is the sampling of gases. The modern trend toward the purchase of coal on specifications lends peculiar value to such a chapter.

For technical use, many of the methods given are too long and cumbersome; for example, methods for the absorption of hydrogen by palladous chloride solution or by a solution of colloidal palladium with sodium picrate. Many of the methods given, furthermore, have not been verified by the author and their reliability is questionable. The ammoniacal nickel cyanide method, presented in detail, for the determination of benzene in illuminating gas is one of several instances deserving such criticism.*

The work does not enter the field of mine gases, or of ventilation and air analysis. It merely touches the subject of natural gas.

Some inaccurate statements appear: e. g. (p. 22), that burettes do not usually need calibration for technical work; (p. 172) that natural gas contains small amounts of oxygen and unsaturated hydrocarbons; (p. 57) that among a number of the paraffin hydrocarbons present in a gas any two may be determined by calculation from the results of combustion; and (p. 203) that a white ash from coal indicates high melting point. Among the few typographical errors, a particularly startling one appears on page 232 in the statement "the gas which disappears is oxygen in the proportion of one molecule for each 4 grams of hydrogen." It is to be assumed that "gram-molecule" is here meant, instead of "molecule." Under the heading of ash in coal, an erroneous impression is given that all coal contains sulphur in the form of sulphates to an extent "varying from a few tenths up to 1 percent." The possibility of contamination of coal samples by abrasion of iron surfaces or of flint pebbles in grinding should have been mentioned.

It is unfortunate that probable inaccuracies, such as the reporting of the presence of hydrogen and carbon monoxide in natural gas in the table on page 173, should be quoted from other authorities and their acceptance by the reading public thus promoted.

A number of convenient tables are added in the appendix. The book will find its most useful application in classes of advanced students of fuel engineering.

HORACE C. PORTER

DER KOLLOIDE SCHWEFEL. Von SVEN ODÉN. Nova Acta Reglae Societatis Scientiarum Upsaliensis. Ser. IV, Vol. 3, N. 4. Upsala: Akademische Buchhandlung A.-G. 1913. pp. 193.

This is an exhaustive monograph on the history and properties of colloidal sulphur in which the author includes the results of three years of his investigation of this substance. One of the most important points relating to the author's work contained in the monograph is the working out of a method of "fractional coagulation" which permitted the preparation of a colloidal solution containing particles of practically the same size. It was not until this was done that it was possible to make a satisfactory study of the substance. The monograph also contains a list of references to articles on colloidal sulphur which is an important addition.

J. C. W. F.

IN CONCLUSION

As stated in the November number THIS JOURNAL now ends its existence as a separate publication and, beginning in January, 1914, it will become a part of the *Journal of the American Chemical Society*. A few words concerning this change seem called for here. First, as to how the AMERICAN CHEMICAL JOURNAL came to be established. In a notice referring to the death of Professor James D. Dana, which appeared in Vol. 17, 470 (1895), the editor said: "Up to the year 1878 the present writer had sent his chemical articles to the *American Journal of Science and Arts*, and they had been kindly received. In the year named, however, a number of articles were sent in together and, in the course of a few days, they were returned with a long and extremely friendly letter from Professor Dana, in which he made it clear that he could not publish the articles without entirely changing the character of his journal; and, at the same time, he strongly urged the starting of a chemical journal. The letter led to correspondence which resulted in the foundation of THIS JOURNAL, the first number of which appeared in April, 1879. The editor of the new journal was entirely inexperienced in the work that devolved upon him, and he owes much to the wise counsel and friendly coöperation of Professor Dana."

At first, six numbers a year were published and there were many times when there was difficulty in filling these. By 1889 the supply of material had increased to such an extent as to lead to an enlargement. After this for seven years eight numbers a year were issued. Beginning in 1896, ten numbers a year were issued; and, finally, beginning in 1899, the journal

became a monthly publication, and even then it was found difficult at times to take care of all the material that was sent in.

In the meantime the American Chemical Society has grown to great importance and is amply prepared to provide for the publication of all articles on chemical subjects likely to be prepared in this country. It is certain that if such a society had been in existence in 1878 the AMERICAN CHEMICAL JOURNAL would not have been started. Taking everything into consideration it now seems best to the editor to place the control of his journal in the hands of the society. It is needless for him to say that after thirty-five years of editorial work he does not now withdraw from it without a feeling of deep regret. His earnest hope is that the step may prove wise.

In this connection he wishes to give special thanks to his colaborer, Dr. Charles A. Rouiller, Assistant Editor, who for several years past has borne the principal burden of the work of editing.

I. R.

GENERAL INDEX TO VOLUMES XXI-L

A general index to Volumes 21-50, inclusive, of the AMERICAN CHEMICAL JOURNAL, will be issued early in 1914. Orders should be addressed to the Johns Hopkins Press, Baltimore, Md. Price, \$1.50.